Carbon corrosion of proton exchange membrane fuel cell catalyst layers studied by scanning transmission X-ray microscopy

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HIGHLIGHTS

- STXM is used to analyze polymer membrane fuel cell cathodes.
- Carbon corrosion and Pt-in-membrane degradation is tracked.
- Low surface area and medium surface area carbon supports are compared.
- Ionomer, Pt and carbon support are quantitatively mapped.
- F 1s and S 2p results show ionomer still present despite extensive C-corrosion.

GRAPHICAL ABSTRACT
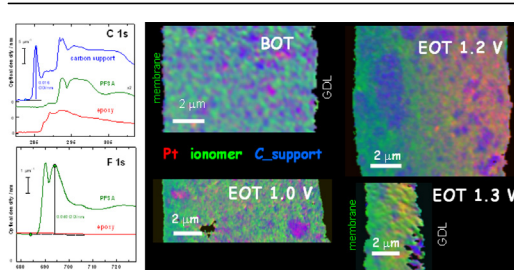
ARTICLE INFO

ABSTRACT

Scanning Transmission X-ray Microscopy (STXM) at the C 1s, F 1s and S 2p edges has been used to investigate degradation of proton exchange membrane fuel cell (PEM-FC) membrane electrode assemblies (MEA) subjected to accelerated testing protocols. Quantitative chemical maps of the catalyst, carbon support and ionomer in the cathode layer are reported for beginning-of-test (BOT), and end-of-test (EOT) samples for two types of carbon support, low surface area carbon (LSAC) and medium surface area carbon (MSAC), that were exposed to accelerated stress testing with upper potentials (UPL) of 1.0, 1.2, and 1.3 V. The results are compared in order to characterize catalyst layer degradation in terms of the amounts and spatial distributions of these species. Pt agglomeration, Pt migration and corrosion of the carbon support are all visualized, and contribute to differing degrees in these samples. It is found that there is formation of a distinct Pt-in-membrane (PTIM) band for all EOT samples. The cathode thickness shrinks due to loss of the carbon support for all MSAC samples that were exposed to the different upper potentials, but only for the most aggressive testing protocol for the LSAC support. The amount of ionomer per unit volume significantly increases indicating it is being concentrated in the cathode as the carbon corrosion takes place. S 2p spectra and mapping of the cathode catalyst layer indicates there are still sulfonate groups present, even in the most damaged material.

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1. Introduction

Fuel cell durability has been identified as a key barrier to proton exchange membrane fuel cell (PEM-FC) commercialization. A major

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factor contributing to the performance loss is the stability of the Pt catalyst and catalyst support. These factors are greatly influenced by operational conditions and the structure and composition of the catalyst layer and thus they are a major issue affecting the lifetime of the fuel cell, especially in automotive applications [1—6]. One of the operational conditions that is recognized as a major cause for voltage degradation is the shut-down/start-up condition of the fuel cell stack, where a H_2/air front in the anode can result in localized high cathode potentials. The catalyst, typically Pt or a Pt-alloy, is in the form of highly dispersed nanoparticles (2—4 nm) distributed over a carbon support, which consists of a dense but pore-filled network of particles (20—50 nm) that forms a conductive and porous structure. Platinum catalysts on different carbon support materials have been evaluated to identify those optimal for PEM-FC use. In this work, PEM-FC membrane electrode assemblies (MEAs) were prepared using two different types of Pt catalyst carbon support materials — a low surface area carbon (LSAC) and a medium surface area carbon (MSAC). The objective of this study was to understand the effect of high voltage excursions, which are typically encountered during start up/shut down operation, on cathode catalyst layer degradation mechanisms for Pt catalysts supported on LSAC and MSAC supports. We have applied soft X-ray scanning transmission X-ray microscopy (STXM) [7—9] to ultramicrotomed thin sections of MEAs in order to measure quantitative chemical maps of the constituent components, in particular the Pt catalyst, the ionomer and the carbon support in the cathode layer, using methods developed and described elsewhere [10—13]. STXM was applied to beginning-of-test (BOT) samples and to various types of end-of-test (EOT) samples that were subjected to different accelerated testing protocols.

Scanning transmission soft X-ray microscopy (STXM) [7—9] is a synchrotron based analytical microscopy that uses the natural X-ray absorption properties of the chemical species present to provide molecular speciation (i.e. bonding as well as elemental identification) and quantitative analysis at high spatial resolution (∼30 nm routine, state-of-art is 10 nm [14]). For the past 5 years our group at McMaster University and others have been applying soft X-ray STXM methods to investigate a range of properties of PEM-FC materials [10—13,15—19]. Here we use STXM to investigate the changes in morphology, chemical composition and spatial distributions of components in PEM-FC MEAs caused by various testing protocols. A focus of the study was to probe the influence of the type of catalyst support (LSAC or MSAC) that was used in the two classes of PEM-FCs on catalyst layer compositional degradation. The major degradation phenomena in these tests was Pt agglomeration in the electrode, Pt migration into the membrane
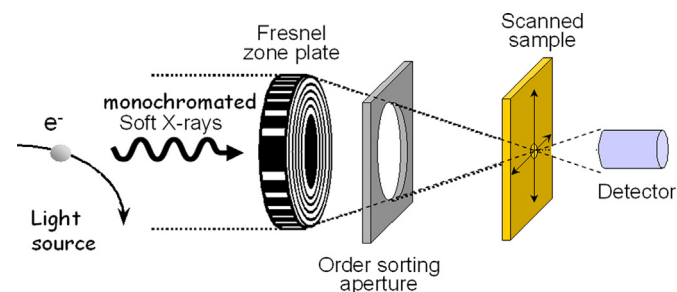
(PITM), and carbon corrosion, i.e. physical loss of carbon support material.

This paper is organized as follows. The experimental section describes the samples and the accelerated testing procedures used, the method for STXM sample preparation, and the methods for STXM acquisition and data analysis. The results section starts by presenting the performance of the different catalysts under the accelerated stress testing. This is followed by detailed presentation of the STXM results, first those for the LSAC BOT, then LSAC EOT, followed by those for the MSAC BOT and MSAC EOT samples. Differences in results for the LSAC and MSAC series are discussed. Quantification of the ionomer in all 8 samples from the F 1s edge, and in two samples (LSAC BOT and LSAC EOT_1.3V) from the S 2p edge are reported. The discussion relates the STXM results to the performance and how the degradation differs with the two types of catalyst supports.

2. Experimental

2.1. Sample description and history

Membrane Electrode Assemblies (MEA) were made of a catalyst coated membrane (CCM) using a Pt loading of 0.4/0.1 mg cm^{-2} (cathode/anode), a commercial 50:50 wt.% Pt/C catalyst, and Nafion® ionomer. The CCM was manufactured in-house using the Nafion® NR211 membrane. The gas diffusion layers (GDL) were made by AvCarb using a continuous process. MEAs using two different catalysts were tested to compare the corrosion resistance of carbon supports; a graphitic low surface area carbon (LSAC) support of 180 m^2 g^{-1} surface area (BET) and a slightly less graphitic medium surface area carbon (MSAC) support of 250 m^2 g^{-1} surface area (BET). The test hardware used was designed to provide quasi-uniform operational conditions with the following features: bladder compression, high flow rates, liquid cooled temperature control, and carbon composite plates with parallel flow fields designed for low pressure and uniform flow, and an active area of 45 cm^2.

The cell was conditioned at standard steady state operating conditions prior to accelerated stress testing (AST) which accelerated the degradation of the cathode through voltage cycling under the following conditions: (cathode)/H_2 (anode) environment, voltage cycling from a lower potential limit of 0.6 V_{RHE} for 30 s, to various upper potential limits (UPL) of 1.0—1.4 V_{RHE} for 60 s. Performance diagnostics (polarization, cyclic voltammetry) was conducted after 0, 50, 700, 1400, 2100, and 4700 cycles. Scanning electron microscopy (SEM), X-ray Diffraction (XRD) and STXM analyses were performed on beginning-of-test (BOT) and degraded end-of-test (EOT) MEAs.

2.2. Sample preparation for STXM

The membrane electrode assemblies (MEA) from the BOT and EOT PEM-FC samples were cut into small rectangular (1 mm × 3 mm) pieces and embedded in an epoxy [20]. The embedded samples were cut at room temperature using a Leica Ultracut UCT ultramicrotome (Leica Mikrosystem, Wien, Austria). The nominal (target) thickness of the sections was 100 nm in order to have a peak optical density between 0.5 and 1.5 at the C 1s edge. However, due to the rubbery character of the membrane, the membrane part of the sections was significantly thicker, probably because that part of the sample was cut only on every third or fourth pass of the sample over the diamond blade. Several ultramicrotomed sections were deposited on a 100-mesh formvar-coated Cu TEM grid (∼30 nm thickness of formvar film) [21]. Only sections with a reasonably intact membrane were examined by STXM.

Fig. 1. Schematic of a scanning transmission X-ray microscope (STXM). X-rays produced by a storage ring (the bend magnet at ALS BL 5.3.2.2, or the elliptically polarizing undulator at CLS BL ID10.1) are monochromated by beamline optics and illuminate a Fresnel zone plate. A fraction (10—15%) of the X-rays are focused to a ∼30 nm spot, where the sample is located. The zero-order (non diffracted) X-rays are blocked by the order sorting aperture. Images are acquired by detecting transmitted X-rays in single photon counting mode synchronously with raster scanning the sample.