Failure analysis of fuel cell electrodes using three-dimensional multi-length scale X-ray computed tomography

A. Pokhrel [a], M. El Hannach [a], F.P. Orfino [a], M. Dutta [b], E. Kjeang [a, *]

[a] Fuel Cell Research Lab (FCReL), School of Mechatronic Systems Engineering, Simon Fraser University, 250-13450 102 Avenue, Surrey, BC V3T 0A3, Canada
[b] Ballard Power Systems, 9000 Glenlyon Parkway, Burnaby, BC V5J 5J8, Canada

HIGHLIGHTS

- A 3D multi-length scale approach is demonstrated for failure analysis of electrodes.
- Cracks and thickness are studied at micro scale and 3D structure at nano scale.
- Catalyst layer thinning and porosity reduction shows collapsing of the structure.
- Fuel cell performance losses are correlated to structural observations.

GRAPHICAL ABSTRACT
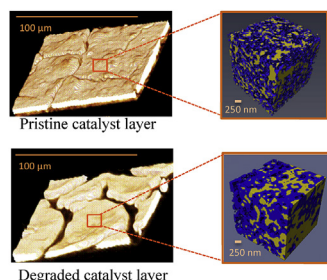
Pristine catalyst layer

Degraded catalyst layer

ARTICLE INFO

ABSTRACT

X-ray computed tomography (XCT), a non-destructive technique, is proposed for three-dimensional, multi-length scale characterization of complex failure modes in fuel cell electrodes. Comparative tomography data sets are acquired for a conditioned beginning of life (BOL) and a degraded end of life (EOL) membrane electrode assembly subjected to cathode degradation by voltage cycling. Micro length scale analysis shows a five-fold increase in crack size and 57% thickness reduction in the EOL cathode catalyst layer, indicating widespread action of carbon corrosion. Complementary nano length scale analysis shows a significant reduction in porosity, increased pore size, and dramatically reduced effective diffusivity within the remaining porous structure of the catalyst layer at EOL. Collapsing of the structure is evident from the combination of thinning and reduced porosity, as uniquely determined by the multi-length scale approach. Additionally, a novel image processing based technique developed for nano scale segregation of pore, ionomer, and Pt/C dominated voxels shows an increase in ionomer volume fraction, Pt/C agglomerates, and severe carbon corrosion at the catalyst layer/membrane interface at EOL. In summary, XCT based multi-length scale analysis enables detailed information needed for comprehensive understanding of the complex failure modes observed in fuel cell electrodes.

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1. Introduction

The commercial durability requirements of polymer electrolyte fuel cells vary significantly and range from 5,000 h for cars to 40,000 h of continuous operation for stationary applications [1]. Currently, achieving fuel cell lifetime targets is a challenge in part due to electrode degradation and associated fuel cell performance losses over time. This lifetime duration can be improved by understanding catalyst layer degradation, identifying failure modes, and applying mitigation strategies.

* Corresponding author.
E-mail address: ekjeang@sfu.ca (E. Kjeang).

The catalyst layer structure can be described as a collection of agglomerates [2] composed of interstitial pores [3] and carbon supported platinum particles surrounded by ionomer. The pore size and structure are critically important for adequate mass transport of reactant gases and product water to and from the active sites. The pore size distribution depends on the fabrication process and catalyst layer composition. For example, a more uniform pore distribution has been achieved for the screen printing method which disperses catalyst agglomerates more uniformly than the spraying method, contributing to improved mass transport of reactant gases and water [4]. It has been shown that the addition of ethylene glycol to the catalyst slurry formulation helps in enhancing the formation of secondary pores in the catalyst layer, which improves performance [5]. In addition, a typical composition of 40 wt% Pt/C in the cathode catalyst layer yields the best overall fuel cell performance when compared to 20, 60, and 80 wt% Pt/C [6].

Catalyst layer degradation can be summarized as a degradation of the individual solid phases of the catalyst layers; i.e., ionomer, platinum, and carbon. The ionomer degradation in the catalyst layer is caused by hydrogen peroxide, hydroxyl radicals, and other contaminants. The presence of platinum close to the ionomer will scavenge some of the contaminants hence ionomer contamination is likely to be less significant than in the membrane [7]. However, the generation of water in the ionomer might cause the ionomer to degrade more than the membrane [8].

The platinum degradation in the catalyst layers is caused by platinum agglomeration and particle growth, platinum loss and migration, and contamination of the active sites [9]. Platinum agglomeration, a failure mechanism in the catalyst layer, occurs after platinum particles get detached from the carbon support due to carbon corrosion and combine to form larger platinum particles to reduce the high surface energy [10]. Additionally, some of the smaller platinum particles dissolve, diffuse, and redeposit into larger particles via Ostwald ripening, resulting in a reduced electrochemical surface area (ECSA) which causes a fuel cell voltage drop.

Some of the platinum in the catalyst layer also migrates to the proton exchange membrane (PEM) where it is deposited in the form of a platinum band and is described in the literature as platinum in the membrane (PITM). The redistribution of platinum particles in the membrane involves a process of platinum dissolution, formation of Pt^+ species, migration into the membrane, and reduction of Pt particles by H_2 [10]. Contaminants present in the fuel and/or air such as CO, CH_4, CO_2, NH_3, NO, and system derived contaminants (metallic ions or silicon) can cause platinum surface poisoning; for example, by forming a CO layer limiting the adsorption of H_2 onto the active Pt area and decreasing the activity of the catalyst layer [10].

The carbon support in the catalyst layers, over time, suffers from severe microstructural degradation. When PEM fuel cells are operated at high temperatures for a prolonged period, at high water content, low pH, and high oxygen concentration, the carbon support is prone to degrade both physically and chemically [10], giving rise to carbon oxidation or carbon corrosion, a dominant catalyst layer failure mechanism. Among factors such as potential, relative humidity, and carbon surface area, higher potential is the most aggressive factor to induce carbon corrosion. For example, significant surface oxidation of Vulcan carbon support has been observed at potentials greater than 1.0 V at room temperature [11]. Carbon corrosion can also occur during normal operating potentials, at the air and hydrogen boundary, and from fuel starvation at the anode. However, carbon corrosion is minimal under normal operating potential. During the fuel cell startup and shut down cycle, the presence of oxygen at the anode due to gas crossover through the membrane and the formation of oxygen and hydrogen boundary will create a carbon oxidation reaction at the cathode resulting in carbon corrosion [10]. Finally, fuel starvation at the anode increases the anode potential to a higher value than the cathode thus inducing carbon corrosion as well [12].

In literature, carbon corrosion has been investigated using focused ion beam and scanning electron microscopy (FIB/SEM) by studying the changes in pore structure and porosity after a membrane electrode assembly (MEA) was subjected to potential cycling (24,000 cycles, 0.6 V - OCV) and start/stop cycling (1000 cycles) stress tests [13]. The potential cycled cathode maintained the initial fuel cell performance [13], whereas the start/stop cycling showed a significant amount of carbon corrosion leading to a poor fuel cell performance. In a separate study, substantial thinning in the cathode catalyst layer was seen after an MEA was subjected to potential cycling with a higher upper potential [14]. It was observed that the primary failure mechanism shifted from platinum dissolution to carbon corrosion at potentials higher than 1.2 V.

Mechanical damage also causes catalyst layer degradation and can appear as flaws or mud-cracks and delamination between the carbon-catalyst agglomerate and the electrolyte. Cycling from hygro-thermal stresses due to the operating conditions of fuel cells in vehicles results in mechanical damage or degradation [15]. The cracks on the catalyst surface can lead to increased resistance within catalyst layers, flooded areas, and areas susceptible to catalyst erosion [16]. Previous research studies have shown that catalyst layers with higher catalyst crack area show higher carbon corrosion degradation [17]. Hence, the structural characterization of the catalyst layers in the MEA is very important in order to understand its degradation mechanisms in fuel cells. Scanning electron microscopy (SEM) is a widely used technique to characterize catalyst layer cracks and thickness, primarily by two-dimensional, cross-sectional imaging of the MEA. SEM has been used to show cracks in the catalyst layer which are caused by the MEA manufacturing processes (solvent evaporation, poor membrane handling, bending or stretching of the MEA) or electrolyte swelling during hydrated fuel cell operation [16]. However, the SEM operates in vacuum, which will cause dehydration of the ionomer in the catalyst layer, resulting in morphological artifacts. In addition, sample damage can occur from the charged particles used in electron imaging techniques such as SEM and transmission electron microscopy (TEM). The challenge increases significantly as the MEA degrades and the catalyst layers intermingle with other layers in the MEA and become difficult to separate. Even if the layers were to separate, the samples might be altered chemically and structurally. A technique which helps overcome these challenges and allows one to study the catalyst layer structure and properties nondestructively is X-ray computed tomography (XCT). XCT also enables reconstruction of three-dimensional images for more comprehensive analysis than what is possible from two-dimensional views.

At the micro length scale, XCT has been used to visualize the morphology and uniformity of fuel cell electrodes prepared by different fabrication methods [18], while at the nano length scale, XCT has been used to extract the volumetric distribution of the effective secondary pores, carbon support agglomerate diameters, and pore size distribution in the catalyst layer [19]. In order to attain a comprehensive understanding of catalyst layer failure modes, an investigation at both of these length scales is desirable.

The objective of the present work is to qualify the multi-length scale approach enabled by the XCT technique for 3D failure analysis of *in situ* degraded fuel cell electrodes. Analysis and comparison of beginning of life (BOL) and end of life (EOL) MEA images at the micro and nano scales is expected to provide an extensive understanding of catalyst layer degradation in fuel cells which complements *in situ* diagnostics such as fuel cell performance, ECSA, and