Statistical structure-to-property relationships for fuel cell materials

K. Artyushkova¹, A. Patel¹, P. Atanassov¹, V. Colbow², M. Dutta², D. Harvey² & S. Wessel²

¹*Chemical and Nuclear Engineering, University of New Mexico, USA*

²*Ballard Power Systems, Burnaby, BC, Canada*

Abstract

Development and optimization of components for fuel cells is hindered by the complex nature of the materials, a partial understanding of the reaction mechanisms and precise chemistry of active site or sites and relationship between performance and morphological properties such as size of particles, surface area, roughness, porosity, etc. XPS is one of the most widely utilized surface spectroscopic techniques for the analysis of material structure. Surface morphology is one of the most important factors affecting functional performance of fuel cell components. Correlation of structure, morphology and performance of Pt catalysts within MEA subjected to different accelerated test protocols (AST) is achieved through the application of principal component analysis (PCA) to curve-fits of high-resolution XPS spectra combined with morphological parameters extracted from SEM images and results of electrochemical measurements.

Keywords: structure-to-property correlation, X-ray photoelectron spectroscopy, SEM, morphology, digital image processing, durability, fuel cells, electrocatalysts, principal component analysis.

1 Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) are a promising alternative energy source, capable of being deployed as successful replacements in many stationary and mobile applications. Durability of catalyst layer (CL) is of key importance in the large-scale deployment of PEMFCs.

Accelerated stress tests (ASTs) have become the standard for PEMFC aging protocols [1, 2]. Using ASTs researchers are capable of aging the cells at more rapid rates than they would typically achieve in standard operation.

For Pt supported on carbon catalysts, CL degradation is linked to Pt dissolution and agglomeration, ionomer degradation, carbon support degradation, and the changes in pore morphology and surface properties [3–5]. X-ray photoelectron spectroscopy (XPS) is a powerful technique to study the chemical changes in the catalysts layers and polymer membrane.

The quantitative information contained in SEM images is largely underutilized with qualitative analysis being a preferred approach. However, digital image processing (DIP) of SEM images is able to convert the 2-D intensity distribution into 1-D image descriptors (values) that can be utilized for quantitative morphology analysis. A major difficulty in direct correlation between morphology and functions of materials is the lack of information on the scale of surface topography and the texture that are responsible for different functions of the materials. Different phenomena and processes related to the material performance correspond to different diffusion regimes at different length scales. Therefore, it is important to access these multiscale morphological features of materials.

The objective of this study was to characterize physical and chemical changes of aged MEAs, and to correlate these changes to perceived performance losses. Multiple carbon support materials were tested as cathode catalysts for MEAs. These MEAs were cycled using AST protocols in order to rapidly degrade the cathode catalyst. Conditioned and aged catalysts coated membranes (CCMs) were then analyzed using XPS, to quantify chemical structural changes, and SEM to quantify morphological changes. These data sets were then processed using PCA in order to draw statistical correlations between the chemical, physical, and performance changes observed.

2 Experimental details

2.1 Materials

In order to understand the effect of the carbon support on catalyst degradation, Pt catalysts on different carbon supports, low surface area (LSA), mid-range surface area (MSA), high surface area (HSA) carbons and in addition, heat treated high HSA surface area carbon (HSAHT) Pt catalyst, each with 50wt% Pt, were investigated. CCMs including following catalysts with 0.4 mgPt/cm² Pt loading were studied: Pt50LSAC, Pt50MSAC, Pt50HSAC1, Pt50HSAC1-HT, Pt50HSAC2, and Pt50HSAC2-HT. The anode portion of the membrane used Pt50LSAC at a loading of 0.1mgPt/cm², and membrane was Nafion® NR-211.

2.2 MEA testing

MEAs were operated at 80°C, 100% RH with 5 psig back pressure of hydrogen and air on the anode and cathode sides, respectively. The cells were run at high

stoichiometric ratios. The MEAs were conditioned overnight by being held at a current density of $1.3\text{A}/\text{cm}^2$. Following the conditioning step, the BOL polarization curves for the membranes were obtained. The fuel cells were then cycled from 0.6V for 30s to 1.2V for 60s. MEAs using Pt50LSAC as the cathode, however, were subjected to additional cycling protocols which changed the upper potential limit (UPL) to 1, 1.3, 1.4V or 1.6 V (vs. RHE). Irrespective of which AST protocol was used, the cells were cycled 4700 times.

2.3 XPS analysis

Conditioned and aged CCMs were analyzed using a Kratos Axis DLD Ultra spectrometer using monochromatic Al $K\alpha$ X-ray source, with emission voltage of 15 kV and emission current of 10 mA. High resolution spectra for carbon, fluorine, oxygen, and platinum were acquired to determine to what extent chemical shifts had altered the carbon support, platinum nanoparticles, or Nafion[®] ionomer.

2.4 SEM and digital image processing

SEM images were acquired for conditioned and degraded CCMs. The images were taken at 2.5K and 50K magnification at a voltage of 1kV. Multiple locations were chosen per sample, and the locations were chosen randomly in order to prevent user bias from influencing the results. The images were analyzed through Digital Image Processing software to quantify changes to sample morphology due to conditioning and accelerated stress testing.

3 Results and discussion

3.1 XPS results

XPS provides chemical composition from top 5–10 nm of the material. High resolution C and Pt spectra were curve-fit using individual symmetrical peaks to derive speciation information. Figure 1 shows changes in speciation as a function of UPL of AST for Pt50LSAC CCM sample. The C1s speciation obtained by cycling the cell to a maximum of 1V gave identical results to cycling the CCMs to 1.2V, however subjecting the cells to higher potentials resulted in drastically different composition. At 1.3V and 1.4V, the amount of graphitic carbon from the carbon support and fully fluorinated carbons from ionomer, CF_2 , decreased, while the carbonate and carboxylate species increased. These results suggest oxidation of both carbon of the catalyst support and of the ionomer.

Moreover, cycling Pt50LSAC resulted in significantly lower PtO and Pt-C content while the metal form of platinum increased. Though the carbon speciation for the 1V and 1.2V AST protocols were identical, there were differences in the platinum speciation. These were manifested by detachment of Pt associated with C and growth of Pt particles resulting in larger amount of metallic Pt.

Figure 1: Changes in relative % of carbon and Pt species for Pt50LSAC sample as a function of UPL AST potential.

3.2 SEM results

Figure 2 shows SEM images for conditioned and aged CCMs at two different magnifications. Careful consideration was taken to ensure that the magnification, voltage, brightness, and contrast were at constant values for all images. From Figure 2, it is clearly visible that the structure of material has changed drastically following the cycling protocol. The corroded sample no longer shows individual carbon black particles that are clearly visible in the conditioned CCM image.

Figure 2: SEM images of conditioned, aged and corroded CCM at 2.5K (top row) and 50K (bottom row) magnifications.

Even though through visual inspection of SEM images, major changes in morphology are obvious, much more morphological details are contained within the images that are not obvious to a human eye. In order to understand impacts of AST on roughness, porosity and texture of CCMs, digital image processing of SEM images were performed [6, 7]. For this study we focused on skewness (Rsk) as it describes asymmetry of the roughness, pointing to the domination of pores or peaks in the image. Its value increases as amount of pores (dark values of intensity within images) increases.

Figure 3: Sample images and line profiles for overall image and their separated waviness (low-frequency) and roughness (high-frequency) components.

A typical surface exhibits roughness superimposed over waviness. Waviness is due to the more widely spaced repetitive deviations (low-frequency component of images) and roughness is due to the finer irregularities of surface roughness (high-frequency component of images). It is important to separate and evaluate waviness and roughness parameters individually. For this purpose, we have applied high-pass filter to remove low-frequency component and low-pass filter to remove high-frequency component from images to produce roughness and waviness image components, respectively [7].

Figure 3 shows image components, and corresponding line profiles, from which skewness was calculated separately by filtering of SEM images acquired at 2.5K magnification. At this magnification, high-frequency component images

correspond to roughness in the range of 0.4–1 μm , and low-frequency component images correspond to 5–20 μm . The same has been done for images at 50K magnification. At this magnification, filtering separates images into low-frequency components at 0.2–1 micron scale and high-frequency component at 20–100 nm. Figure 4 shows hierarchy of scales extracted from SEM images. Because images were acquired at 2 different magnifications, the high frequency and low frequency components porosity represent two length scales with the high frequency components at 2.5K being approximately the same length as the low frequency components at 50K magnification.

Figure 4: Profiles extracted from SEM images by filtering shown at scale.

Figure 5 shows skewness parameters extracted from image components separated by filtering. Overall skewness and skewness at scale of 5–20 microns does not change significantly with increasing AST potential. Dramatic increase in porosity as represented by skewness at scales of 0.2–1 microns and 20–100 nm is detected as UPL of cycling increases. In comparison with conditioned sample, the porosity at larger scale of 5–20 microns increases for all tested samples. Degradation of MEA, however, is linked mainly to changes at scale from tens of nanometer up to a micron. This microroughness and microporosity introduced plays a significant role in water management, potentially, causing failure of MEAs at higher UPL of cycling.

To get an additional insight into the mechanism of MEA degradation for classes of different types of carbons used as supports, multivariate analysis, particularly, Principal Component Analysis was applied to the data combining structural, morphological and durability parameters shown in Table 1.

Figure 5: Skewness parameters, overall, low and high frequency from 2.5K and high frequency for 50K SEM images as a function of AST potential.

Figure 6: PCA biplot from data in Table 1.

These parameters combine relative % of carbon and Pt species, such as plotted in Figure 1, skewness parameters extracted from SEM images, such as plotted in Figure 5, Pt particle size obtained from TEM of cycled MEAs, % thickness change, loss in V at 0.3 A/cm² and Electrochemically Accessible

Surface Area (ECSA). The sample set include Pt50LSAC at various UPL of AST cycling and 4 high surface area carbon-based catalysts, HSAC, original and heat treated.

Table 1: All data for statistical structure-to-property correlations.

	ECSA	Pt size	Thickness Change	Loss in V: 0.3 A/cm ²	R _{sk}	R _{sk} ^H	R _{sk} ^L
LSAC 1.0 V	75.0	8.5	1.1	11.5	1.05	0.18	1.02
LSAC 1.2 V	73	8.1	0.0	24.0	1.04	0.19	1.02
LSAC 1.3 V	51	8.6	8.8	138.2	1.07	0.08	1.04
LSAC 1.4 V	18	7.5	9.5	161.1	1.15	0.14	1.05
LSAC 1.6V	68	7.7	8.9	57.3	1.14	0.40	1.10
HSAC2 1.0 V	132	6.5	0.7	39.4	1.07	-0.07	1.01
HSAC2 1.2 V	21	10.1	7.6	361.9	1.14	0.20	1.06
HSAC1 HT 1.2	65	9.5	1.8	21.6	1.08	0.00	1.04
HSAC2 HT 1.2	9	10.1	9.1	357.0	1.19	0.33	1.07

	COOH	CO ₃	CF ₂	Pt	Pt-C	PtO
LSAC 1.0 V	3.1	3.3	19.6	57.8	29.0	13.2
LSAC 1.2 V	3.7	5.3	23.3	60.3	27.9	11.8
LSAC 1.3 V	7.1	21.3	14.7	62.4	22.6	15.0
LSAC 1.4 V	10.3	25.5	14.5	62.4	23.2	14.4
LSAC 1.6V	7.3	27.6	14.7	58.0	34.3	7.6
HSAC2 1.0 V	3.3	2.4	14.0	53.7	26.2	20.2
HSAC2 1.2 V	9.8	20.6	14.6	62.7	26.6	10.7
HSAC1 HT 1.2	4.0	5.7	25.6	59.6	29.6	10.8
HSAC2 HT 1.2	5.3	20.1	18.9	64.4	21.8	13.8

Figure 6 shows PCA results. Non degraded aged MEA samples, LSAC cycled at 1.0 and 1.2 V, HSAC 2 sample cycled at 1.0 V and HSAC 1 HT cycled at 1.2 V show larger retained ECSA correlated with smaller loss of Pt associated with C and oxides. Severally degraded samples, those showing larger loss in voltage, being LSAC tested at all voltages higher than 1.2 V and HSAC2 samples original and heat-treated tested at 1.2 V have larger amounts of carboxylates and carbonates and metallic Pt correlated with larger Pt size. Thickness change is being accompanied by larger porosity at all scales as provided by DIP of SEM images.

Figure 7 shows direct correlations between the parameters highlighted by statistical structure-to-property correlations obtained via PCA. Increase of relative % of metallic Pt as determined by XPS is correlated with the size of Pt particles as determined by TEM. The relative % of Pt-O and Pt associated with carbon retained after testing is correlated with larger ECSA. Increase in surface oxides such as carbonates and carboxylates is linearly related to the loss in performance as manifested by loss in the V at constant current. And finally, change in thickness of CL is associated with total increase in porosity as calculated by DIP of SEM images.

Figure 7: Correlation between structural, morphological and performance parameters for all types of catalysts.

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