

Structural and Morphological Properties of Carbon Supports: Effect on Catalyst Degradation

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Abstract

The object of this work was to identify correlations between performance losses of Pt electrocatalysts on carbon support materials and the chemical and morphological parameters that describe them. Accelerated stress testing, with an upper potential of 1.2 V, was used to monitor changes to cathode properties, including kinetic performance and effective platinum surface area losses. The structure and chemical compositions were studied using X-ray Photoelectron Spectroscopy and Scanning Electron Microscopy coupled with Digital Image Processing. As this is an ongoing study, it is difficult to draw firm conclusions, though a trend between support surface area overall performance loss was found to exist.

Introduction

The commercialization and overall acceptance of polymer electrolyte membrane fuel cells (PEMFCs) in today's market place face two great challenges: minimizing cost and maximizing durability. These challenges are firmly related, and an effort to improve one, by its very nature, works to improve the other. Currently, a great deal of time and expertise is being spent on fully understanding the degradation processes occurring in a PEMFC, with a particular focus on the catalysts and their support materials.

Because of its low cost and good conductivity, graphitic carbons are often used in PEMFCs as support materials. The performance and corrosion stability of Pt electrocatalysts on morphologically and chemically different carbon supports were investigated in order to understand the effect the support material has on catalyst degradation. Low surface area (LSA), mid-range surface area (MSA), high surface area (HSA), and heat-treated, high surface area (HSA HT) carbons were extensively studied and characterized.

In this study, the carbon support materials were subjected to accelerated stress testing (AST) to monitor performance losses. Electrode Impedance Spectroscopy (EIS) and Cyclic Voltammetry were used to examine cathode catalyst layer changes. The materials were also characterized using X-Ray Photoelectron Spectroscopy (XPS) and scanning electron microscopy (SEM), with the resulting data being processed using Principal Component Analysis (PCA), a Multi-Variate analysis method. Finally relationships were drawn between morphological and chemical parameters with various corrosive behaviors.

Materials and Methods

Materials

In order to understand the effect of the carbon support on catalyst degradation, distinctly different carbon supports, low surface area (LSA), high surface area (HSA), and mid-range surface area (MSA) carbons were investigated. High surface area carbons have a larger number of catalyst anchor sites yielding well-dispersed catalyst particles on the support. This level of dispersal is believed to result in increased kinetic performance. However, the large number of surface sites means these carbons will be more susceptible to corrosion, thus altering their performance and level of degradation. In order to stabilize the high surface area carbon, it was heat treated to cause some degree of graphitization, with the resulting material being labeled HSAHT.

Performance Measurements

In order to evaluate the performance and degradation losses of the Pt electrocatalysts, a wide array of techniques were used. Accelerated stress testing (AST) using an upper potential of 1.2V was used to study the effect of the carbon support on cathode degradation with respect to changes in cathode thickness, effective platinum surface area (EPSA), and kinetic performance. Capacitance measurements were also taken using Electrode Impedance Spectroscopy (EIS). Capacitance is believed to be an indirect measure of carbon corrosion; small changes indicate low levels of corrosion while large changes suggest the opposite.

Characterization

Again, the goal of this work was to relate performance losses to chemical and morphological parameters. As such, X-ray Photoelectron Spectroscopy (XPS) was chosen to obtain information on graphitic content (degree of crystallinity) and surface oxide content of the carbon supports. The ability to discriminate between different carbon chemical environments, not just elemental compositions, is one of the primary advantages of XPS in the characterization of carbon corrosion. Morphological properties such as size of particles, size of particles agglomerates, surface area, roughness, and porosity contribute equally to the corrosion process. Digital Image Processing (DIP) can be applied to SEM and TEM images to extract statistical parameters, such as roughness, particle size distributions, shape parameters, and texture parameters, which all are related to morphology of carbon blacks.

Analysis

This multi-analytical approach provides a large set of variables (structural, physical and microscopic properties) which are related to the corrosion behavior of carbon blacks. Dealing with the large number of variables and finding correlations between them, coupled with classifying the samples, is an important challenge. Multivariate statistical methods of data analysis (MVA) are of critical importance in structure-to-property relationship modeling (*Artyushkova, Pylypenko et al. 2008*). Principal Component Analysis (PCA) is used as a tool to find samples which parameters are globally correlated or anti-correlated, and to facilitate visualization of the variables responsible for the correlations.

Results and Discussion

The effect of the carbon support on cathode degradation with respect to changes in cathode thickness, and EPSA and kinetic performance is presented in Fig.1. The cathode layer thickness, EPSA loss, and subsequently the kinetic loss are least affected for low surface area carbon supports and show substantially higher degradation for high surface area carbons. As expected, catalyst degradation with Pt catalyst supported on high to low surface area carbons follows the trend:

LSA < MSA < HSA HT < HAS

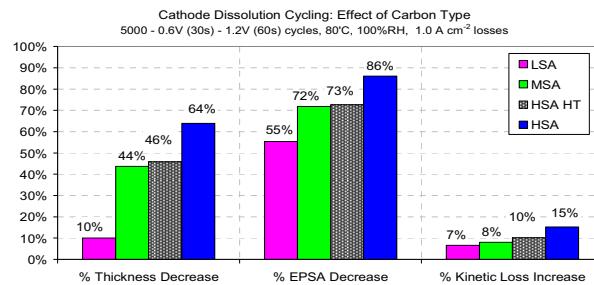


Figure 1: Comparison of Pt supported on various carbon supports subjected to the Pt dissolution AST (UPL-1.2V). Changes in catalyst layer thickness, EPSA, and kinetic performance.

As the Pt particle size and also Pt in the membrane (PITM) was found to be similar for all the tested carbon supported catalysts, the decrease in catalyst layer thickness and EPSA are thus mainly due to carbon oxidation rather than Pt dissolution.

Figure 2a shows the effect of capacitance and high frequency ionic resistance of the catalyst layer with progressive AST cycling. The EIS capacitance is believed to be an indirect measure of carbon corrosion, thus, as expected the low surface area supports show only a small change in capacitance while the medium and high surface area carbons reveal substantial change. The initial increase in capacitance is believed to be due to oxidation of the support surface, such that the surface states are becoming functionalized before the carbon is corroded and results in CO₂ evolution.

Carbon oxidation changes the carbon surface to become more hydrophilic which would result in an increase in bulk proton conduction and/or water movement². The functionalized carbon surface groups may also lead to a secondary proton path in the vicinity of the catalyst particles. Figure 2B illustrates how each carbon's proton resistance changes over time.

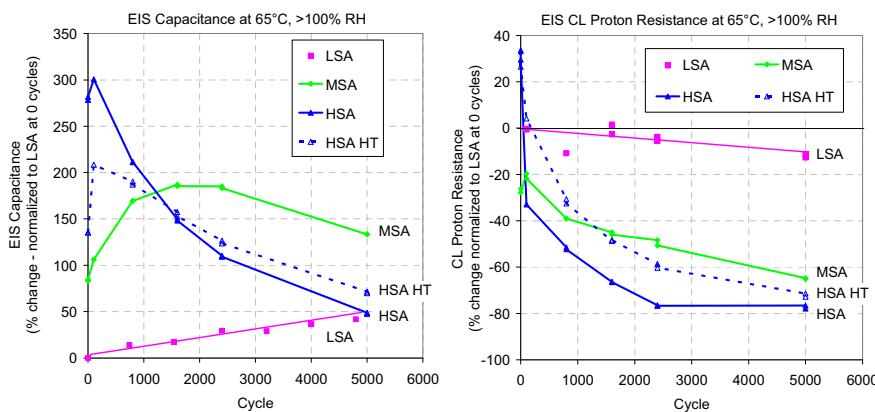


Figure 2: Changes of (A) cathode catalyst layer EIS capacitance and (B) proton resistance (B) as a function of AST cycle number for a variety of catalyst carbon supports

A comparison of voltage degradation for Pt catalysts on different carbon supports is shown in Fig. 3. Consistent with the above discussion, the degradation rates are greater for catalysts with larger carbon support surface areas due to its susceptibility to carbon oxidation and corrosion. The performance degradation will depend on both, current density and initial performance, and number of AST cycles, thus at current densities < 1A/cm² the degradation rate could be substantially lower than those presented in Fig 3.

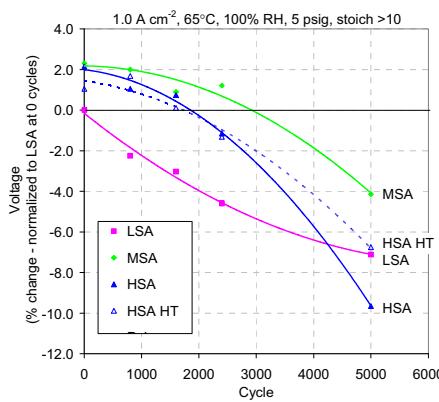


Figure 3: Change in Performance of In-situ PEMFC Pt/C catalysts at 1A/cm², 65°C, 100% RH, 5 psig, stoich >10 with AST cycle number (normalized to LSA performance at 0 cycles)

The performance was found to follow the trend:

$$\begin{aligned} \text{EOL} = 2400 \text{ cycles: } & \text{MSA} > \text{HSAHT} \sim \text{HSA} > \text{LSA} \\ \text{EOL} = 5000 \text{ cycles: } & \text{MSA} > \text{HSAHT} \sim \text{LSA} > \text{HSA} \end{aligned}$$

After collecting the corrosion and performance data, the results needed to be correlated with the physical parameters of the support materials. Table 1 show XPS results for 6 types of carbon blacks and the same carbons decorated with 55% Pt. Low and Medium surface area carbons have the lowest amount of oxygen and, therefore, surface oxides. High surface area carbons consist of approximately 4-5% oxygen, similar to the control

carbon black, Vulcan. Decoration of these carbon blacks with Pt causes significant increase in oxygen for all samples except heat treated HSA carbon. Of the modified carbon blacks, LSA and MSA samples have the highest amount of Pt detected, i.e. 8-9%, close to that observed for Vulcan carbon. The HSA samples still have the highest percentage of carbon and smallest percentage of Pt, but heat treatment causes a significant decrease in both O and Pt content. Three types of Pt are detected for these samples, metallic Pt, PtO and PtO₂. Figure 4 shows the Pt 4f spectra for 2 samples, HSA2 and HSA HT. Platinum composition on LSA and MSA carbons is nearly identical to that on Vulcan. HSA carbons result in catalysts with smallest relative amounts of metallic Pt and largest amounts of Pt monoxide. Heat treatment doubles the relative metallic Pt content

	CBs		Pt on CBs			Pt	PtO	PtO ₂
	C %	O %	C %	O %	Pt %	71.4	72.3	73.2
LSAC	99	1	80.5	11.1	8.4	39.1	22.9	38
MSAC	98	2	81.9	9	9.1	41.4	22.5	36.1
HSAC 1	94.7	5.3	85.2	9.1	5.8	37.6	35.4	27.1
HSAC 2	96.2	3.8	85.9	8.6	5.5	35.4	34.9	29.7
HSAC HT	96.3	3.7	93.1	3	3.9	70.3	20.5	9.2
Vulcan	93.7	6.3	72.4	17.6	10.1	41.6	22	36.4

Table 1: Elemental Composition of Catalyst Supports With and Without Catalyst Along with Content of Pt Species

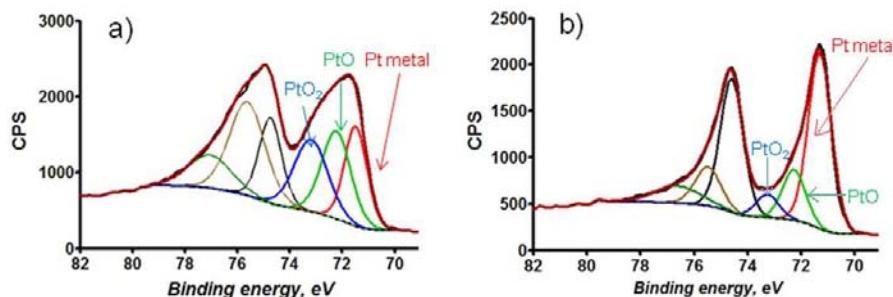


Figure 4: High resolution Pt 4f spectra for a) HSA2 and b) HSA HT samples. Increase in metallic content upon heat treatment is detected.

Scanning Electron Microscopy (SEM) images have been acquired to obtain morphological information for carbon black and Pt-decorated samples. Figure 5 shows representative SEM images for low, medium and high surface area carbons along with SEM images from Pt-decorated samples.

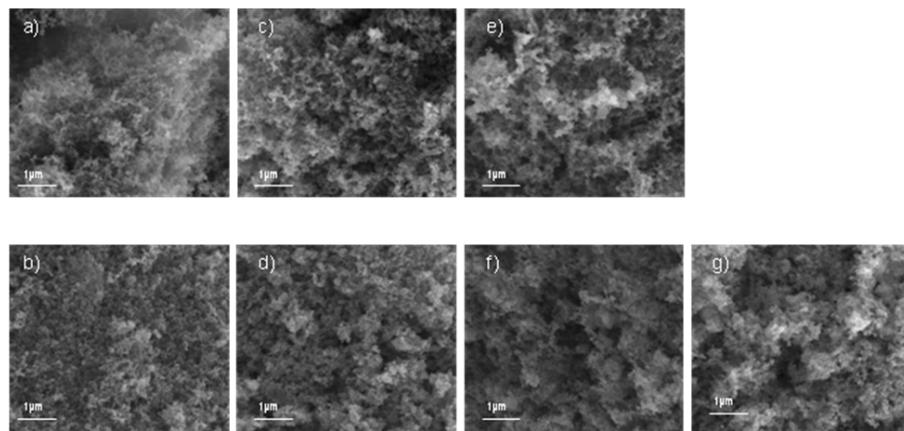


Figure 5: SEM images for carbon blacks a) LSA, c) MSA and e) HSA and Pt-decorated samples b) LSA, d) MSA, f) HAS and g) HAS HT samples.

Changes in morphology and porosity are, to some extent, obvious from visual inspection of the images, but quantitative information is required for a clear understanding of the differences between samples and correlating microscopy with performance and surface chemistry. Digital image processing (DIP) was applied to find a representation of the intensity distribution of an image and to convert 2-D images into descriptors that are useful for morphology representation.

Surface roughness is one of the most important statistical parameters which can be extracted by DIP. [1] The average roughness (R_a) is the arithmetic mean of the absolute values of the surface departure from the mean plane. Skewness, R_{sk} , of the roughness profile is also very important as it describes asymmetry of the roughness, indicating the image is being dominated by valleys (pores) or peaks. R_{sk} increases as relative amount of pores (dark values of intensity within images) increases.

A typical surface exhibits roughness superimposed over waviness. Waviness is due to the more widely spaced repetitive deviations (low-frequency component of SEM images) and roughness is due to the finer, random irregularities of surface texture (high-frequency component of SEM images). Waviness and roughness are responsible for different phenomena and processes in the electrocatalyst performance. Roughness due to microporosity (high-frequency roughness) and roughness due to mesoporosity (low-frequency waviness) are responsible for configurational and Knudsen diffusion regimes, respectively. Therefore it is important to evaluate waviness and roughness parameters individually. For this purpose, we have applied a high-pass filter to remove low-frequency component to produce a roughness image. Conversely, by applying a low-pass filter to remove high-frequency components from images, waviness image components can be obtained.

Texture arising from the repetition of local patterns is another very important feature used in DIP. Textural features such as ones based on grey scale co-occurrence matrices provide measures of such notions as contrast, randomness or directionality. [2-3] Homogeneity, contrast (amount of local variation), correlation (linear dependency of grey levels of neighboring pixels) and energy (uniformity) were evaluated for images.

Dealing with the large number of variables and finding correlations between them for the purpose of classification of samples by performance is an important challenge. Multivariate statistical methods of data analysis (MVA) are of critical importance in structure-to-property relationship modeling.[4] Principal Component Analysis (PCA) is used herein as a visualization tool to find samples which are globally correlated or anti-correlated, and to facilitate visualization of the variables responsible for the correlations.

Figure 6 shows PCA biplot for roughness and texture parameters for carbon black samples only.

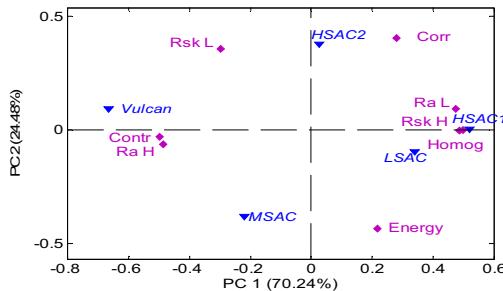


Figure 6: PCA biplot for parameters for carbon black samples

Principal component (PC) 1 captures 70% of variance in the data and separates samples by heterogeneity. HSA and LSA carbons have the largest mesoroughness and number of small pores and are less heterogeneous than the other supports. Vulcan and MSA samples are the most heterogeneous and have the highest contrast, microroughness and number of large pores. Interestingly, SEM images from carbon blacks cannot directly describe surface areas due to signals limited by the sample-air interface.

Figure 7 shows PCA biplot for roughness and texture parameters for Pt-decorated carbon black samples. PC1 is plotted in reverse scale for comparison with classification of carbon black samples in Figure 6. PC1 also captures 70% of the variance in the data and according to classification of variables, separates samples by morphological criteria similar to the ones for undecorated carbon black samples. Pt deposited on Vulcan and Pt deposited on LSA carbon have the highest roughness on both micro- and meso-regimes and the highest contrast. Both HSA carbons have high homogeneity (order) and high porosity due to smaller and larger pores, resulting in higher surface area. The MSA and

HSAHT samples lie on the zero x-axis for PC1, indicating that their morphologies are somewhere in the middle between the two categories discussed.

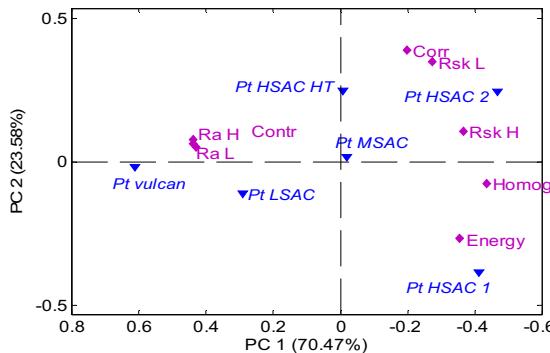


Figure 7: PCA biplot for parameters for Pt-decorated carbon black samples

In this case PC1 is directly proportional to surface area with the contributions in the order of HSAC>MSAC=HSAC HT>LSAC>Vulcan. According to this PCA model, high surface area is related to high porosity in both meso and micro-regimes (Rsk), high energy and homogeneity, and inversely related to high roughness and contrast.

Figure 8 shows the PCA plot for the combined data where roughness and texture parameters from both pure carbon blacks and Pt-decorated samples were augmented by type of carbon blacks. This type of analysis shows how morphological parameters “translate” from carbon blacks upon Pt deposition. Roughness in micro-regime propagates well from carbon to catalysts samples, while roughness in meso-regimes changes dramatically upon Pt decoration, i.e. increasing for HSA samples and decreasing significantly for MSA and Vulcan samples. Porosity in micro-regime captured in Rsk translates upon deposition of Pt, while porosity in meso-regimes changes more for HSA sample.

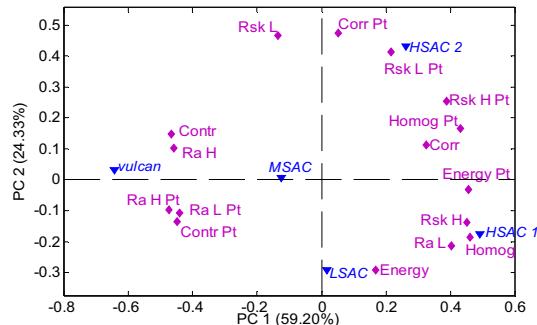


Figure 8: PCA biplot for augmented parameters for pure carbon black and Pt-decorated samples

Next, XPS data in Table 1 were combined with roughness and texture parameters extracted from SEM images for Pt-decorated samples and PCA model was applied (Figure 9).

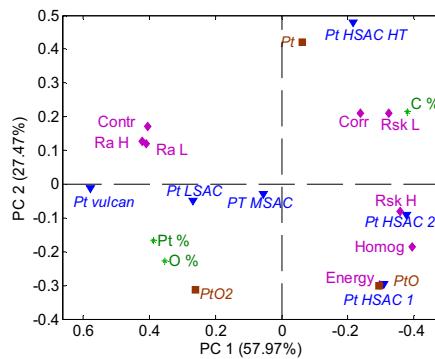


Figure 9: PCA biplot for combined XPS and morphological parameters for Pt-decorated carbon blacks

Samples with lower surface areas have an overall higher content of Pt and O and Pt dioxide, and this is correlated with high roughness in both regimes and high contrast. The heat treated sample had the highest percentages of metallic Pt and overall carbon, and it has a strong correlation in images with highest amount of large pores. High surface area samples have the highest percentages of Pt monoxide and highest content of small pores and are associated with homogeneous morphologies.

Conclusions

Understanding the chemical structure and morphology of Pt electrocatalysts and their supports while linking these parameters to electrocatalytic activity, corrosion stability, and overall performance is essential for elucidating failure mechanisms and optimizing support materials. The strategy presented in this work can be viewed as a universal methodology that allows correlation between multiple variables relevant to fuel cell technology. This study demonstrates that both chemical and morphological (physical) properties of the carbonaceous support contribute to the corrosion stability of catalysts. The detailed quantitative evaluation of those interdependent contributions are a subject of our ongoing research.

Acknowledgments

The authors acknowledge the financial assistance from the Department of Energy EERE Hydrogen and Fuel Cell Technology Program (Project DE-EE0000466) and Natural Resources Canada (Project 414-CETC-526)

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2. R. Borup, et.al. Scientific Aspects of Polymer Electrolyte Fuel Cell Durability and Degradation, Chem. Rev. 2007, 107, 390403951