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Structural correlations: Design levers for performance and durability of catalyst layers

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HIGHLIGHTS

- Chemical and morphological design levers for MEAs are identified.
- Metrics for chemical changes during AST based on XPS spectra is derived.
- Metrics for morphological changes during AST based on SEM images is derived.
- Durability windows of carbon support: graphitic content >55%, surface oxides <15%.

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ABSTRACT

Durability of the catalyst layer (CL) is of vital importance in the large-scale deployment of PEMFCs. It is necessary to determine parameters that represent properties of catalysts layer and other cathode components for optimization of fuel cell performance and durability. The structure, morphology and surface chemistry of the catalyst powder affects the ionomer and catalyst interaction, ionomer dispersion in the catalyst layer and, for this reason, its morphology and chemistry. These, in turn, affect the catalyst layer effective properties such as thickness, porosity, tortuosity, diffusivity, conductivity and others, directly influencing electrode performance and durability. In this study, X-ray Photoelectron Spectroscopy and SEM are used to quantify surface species and morphology of membrane electrode assemblies (MEAs) tested under different accelerated stress test (AST) conditions. Correlations between composition, structure and morphological properties of cathode components and the catalyst layer have been developed and linked to catalyst layer performance losses. The key relationships between the catalyst layer effective properties and performance and durability provide design and optimization levers for making MEAs for different operating regimes.

1. Introduction

Supported platinum-on-carbon catalysts remain the state of the art for fuel cells today, but more information is needed about the factors of activity and durability. Durability is the determining factor in the useful lifetime of polymer electrolyte membrane fuel cell (PEMFC) systems. Fuel cells must be resistant to changes in morphology and surface properties. There are, however, significant changes in catalyst structure and properties during operation.

The U.S. DOE have established durability-test protocols, which includes tests for electrocatalysts, electrocatalyst supports, chemical and mechanical tests of membranes [1]. Ideally, a component designer would like to evaluate new materials and cell performance with a minimum of long-term PEMFC testing. Accelerated stress tests (ASTs) have become the standard for PEMFC aging protocols [1,2]. The use of ASTs has been shown to be very useful for assessing the durability of the PEMFC components. Performance losses and component damages can be more efficiently analyzed under specific working conditions than applying costly and time-consuming steady-state lifetime tests [2]. By analyzing the degradation data of individual cells, Bae et al. illustrated a methodology for estimating the lifetime of the PEMFC stack using the statistical theory of the

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smallest order [3]. The use of segmented cells enabled to understand the origin of local degradations in PEMFC [4].

There is a critical need for creating a set of structural metrics reflecting the properties of catalyst layer components, such as support, catalyst, ionomer, etc., that can be used for sound prognoses of activity and durability. The use of ASTs and the metrics reflecting the performance losses and degradation of components has been widely utilized, but there is a missing link between AST parameters and chemical and morphological changes that occur during ASTs and, what's even more important, there is a lack of a direct relationship between the initial structure of the catalyst layer components and durability metrics used [5].

Surface chemistry and structural morphology of individual components are critical for mass transport properties, water and heat management and subsequently electrocatalytic activity and durability. Carbon is used in fuel cells as an electrocatalyst support to ensure electronic conductivity between the electrocatalyst and the current collector. The carbon support has defects, dislocations, and discontinuities at the edges of layer planes. These defects tend to chemisorb oxygen, giving rise to surface functional groups, which in turn determine the surface chemistry of the carbon blacks. The surface chemistry, in turn, affects the hydrophobicity and thus wetting of products and reactants as well as dispersion in aqueous inks. The topography of real solid surfaces plays an important role in defining the electronic energy distribution at surface sites, particularly when irregularities at the atomic level are taken into account. Likewise, surface irregularities at the nanometric level determine the electrocatalytic properties [6].

The importance, of deriving a set of design criteria for benchmarking potential fuel cell electrocatalysts through ex-situ durability tests assessing stability and degradation processes, cannot be overlooked [7]. The loss of electrochemically active surface area, degree of Pt dissolution, Pt particle growth and carbon oxidation are among most often evaluated parameters [8]. We will discuss the existing understanding related to chemical and morphological properties derived from studies of (1) Pt electrocatalysts; (2) carbon supports and (3) Nafion-based ionomer, as these three represent key components of the catalyst layer in catalysts coated membranes (CCM) [4,5,9,10].

I. *Pt electrocatalyst*. In many studies of PEMFC, it was shown that catalyst degradation is one of the major reasons for gradual performance losses directly related to a loss of accessible surface areas of the active catalyst components. The three fundamentally different mechanisms of loss of electrochemically accessible surface area (ECSA) of Pt are Pt dissolution, the migration and coalescence of Pt nanoparticles on the support, and detachment of nanoparticles from the support [10]. There is a growing consensus that the platinum dissolution is a major factor limiting the lifetime of polymer electrolyte fuel cells, especially under varying load conditions and at the high potentials of the cathode. The analysis of the catalyst after the AST revealed that the well dispersed Pt particles of the original electrode form irregular and branched agglomerates in the catalytic layer [2]. *Ex situ* transmission electron microscopy (TEM) of catalyst layers (CLs) after long-term steady-state and potential cycling operation has shown dramatic changes in platinum particle size and distribution. Two groups of particles were observed in TEM: spherical particles still in contact with the carbon support and nonspherical particles removed from the carbon support. There are also reports on the formation of PtO. X-ray photoelectron spectroscopy (XPS) has provided evidence that Pt(IV) can be formed via oxidation of Pt(II) by hydrogen peroxide.

II. *Carbon support*. Carbon black is widely used as an electrocatalyst support but still suffers from issues that decrease the catalytic activity of the material [9]. In addition to the loss of the platinum, the carbon support that anchors the platinum crystallites and provides electrical connectivity to the gas-diffusion media and bipolar plates is also subject to degradation. Park et al. showed that carbon corrosion leads mainly to Pt detachment and/or Pt coarsening by weakened Pt-support interaction, which results in losses in the Pt surface area and the degradation of the performance of the catalyst [6]. After accelerated stress testing, the aggregates of the carbon black support, which are well defined in the original catalyst, were found to be much more reduced and diffused in the cathode catalytic layer [2]. Carbon oxidation and corrosion was also accelerated by the presence of Pt, and it formed oxygen-containing functional groups, such as C—O and C═O, on the surface of the carbon support as confirmed by XPS [11]. The formation of carbon oxides on the surface of the carbon makes the catalyst layer more hydrophilic and leads to the formation of a thin water film on the surface of carbon, resulting in enhanced proton conductivity within the catalyst layer and decreased mass transport due to possible water flooding of hydrophilic pores. The loss of carbon due to complete oxidation of carbon to form CO_2 may lead to the collapse of the structure of the CLs and a loss of porosity, increasing the mass transport resistance in the CL [6]. Carbon oxidation may cause the crumbling of the carbon catalyst-support and an increase of its roughness together with the loss of platinum. Catalyst nanoparticles can get trapped in the micro-pores and become not accessible to reactants/ Nafion® resulting is a decrease of catalytic activity [12]. A higher graphitization degree of the carbon support leads to an increase in corrosion resistance, but at the same time can reduce the dispersion of platinum on carbon supports [13]. The functionalization of the graphitic carbon was shown to enhance the distribution of Pt nanoparticles and reduce their agglomeration, resulting in higher stability of Pt catalysts with enhanced activity [14,15].

III. *Nafion® degradation.* Avasarala et al. reported the first direct evidence of chemical degradation of Nafion® pendant groups at high cell potential [5]. Prior to that work, the degradation of the main chain through an “unzipping” mechanism was suggested. This reaction could lead to the generation within the membrane of peroxide radicals that attack the Nafion® polymer, both at the chain ends, and at the functional [16]. Cationic pollution can detrimentally affect the properties of ionomer [4]. A recent XPS analysis of Nafion®-112 after ex situ aging in Fenton solution detected loss of fluorine and sulfur from the membrane and the formation of oxygen-rich moieties in the membrane [6].

In the pursuit of developing the micro-structural mitigation strategies for PEM Fuel Cells, we have been involved in extensive characterization work of carbon supports and electrocatalysts of different types [17–19]. 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 [19]. We have subjected carbon supports and supported Pt catalysts to accelerated stress testing to monitor the 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