Electrochemistry Communications 72 (2016) 15–18

Contents lists available at ScienceDirect

Electrochemistry Communications

journal homepage: www.elsevier.com/locate/elecom

Mesoscopic degradation effects of voltage cycled cathode catalyst layers in polymer electrolyte fuel cells

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ARTICLE INFO

Article history:
Received 8 August 2016
Received in revised form 20 August 2016
Accepted 23 August 2016
Available online 25 August 2016

Keywords:
Fuel cell
Durability
Electrode
Catalyst layer
Carbon corrosion
Transmission electron microscopy

ABSTRACT

The first successful imaging of Pt/C and fluorine containing ionomer phases in pristine and degraded cathode catalyst layers is performed using transmission electron microscopy with elemental mapping to investigate the degradation effects caused by high voltage excursions in polymer electrolyte fuel cells. Through high resolution elemental mapping, the distributions of ionomer and Pt/C phases are identified at beginning-of-test. Loss of carbon through corrosion paralleled by Pt and ionomer segregation is diagnosed using elemental maps of the degraded material. The observed fuel cell performance decrement is attributed to the absence of electrically conducting carbon, agglomerated and isolated active platinum, and irregularly redistributed ionomer with a significant mass transport barrier due to voltage cycling.

1. Introduction

The cathode catalyst layer (CCL) is an important component of the polymer electrolyte fuel cell (PEFC) where oxygen is electrochemically reduced. The CCL is usually designed as a porous composite material with Pt nanoparticles supported on carbon black and ionomer, thus providing electrically conductive catalytic sites that facilitate reactant and product transport in the pore and ionomer phases. Catalyst layer degradation, particularly at the cathode, is a major factor contributing to performance loss during PEFC operation [1,2]. The heterogeneous CCL structure may experience irreversible damage from localized non-uniform potential loads, reactant starvation, hot spots, reactant crossover, flooding/washout, and cyclic stresses [3]. Though CCL thinning and crack formation are well known modes of macroscopic degradation [4,5], as often reported from failure analysis, the underlying mechanisms of degradation are not fully established. The most critical knowledge gap exists at the mesoscopic scale, where the molecular level degradation reaction mechanisms are expected to cause structural and compositional changes that are responsible for macroscopic failure of the material in terms of reduced fuel cell performance. Hence, the structural effects of CCL degradation need to be unraveled through spatially resolved imaging of the porous catalyst layer and its constituents.

Cathode degradation was recently explored by electron microscopy through *ex situ* approaches. For instance, startup/shutdown cycles were shown to cause CCL compaction through carbon particle ‘neck-braking’ and embedded Pt particles within the structure which hinder the transport of oxygen and water [6]. X-ray computed laminography results revealed agglomerated areas and enlarged cavities in the CCL after voltage cycling. The degradation mechanism proceeded with Pt dissolution, carbon corrosion, Pt detachment, and agglomeration [7,8]. Identical location electron microscopy identified the local trajectories of carbon and Pt in the process of carbon corrosion, Pt detachment, and Pt sintering on a group of electrocatalyst particles in an *ex situ* setup subjected to voltage cycling [9,10]; however, this technique is not compatible with complete CCL materials in a fuel cell assembly. Though the carbon and Pt phases can be readily imaged through electron microscopy, the ionomer phase is more challenging to capture because of its poor electron scattering. Image contrast can be enhanced by ion-exchange with heavy metals [11,12]; however, the staining element may introduce discrepancies in the interpretation of real solid content. Furthermore, the use of focused-ion beam milling for sample preparation has been shown to cause ionomer melting, carbon amorphization, physical damage, and ion contamination [13]. Hence, alternate approaches in the sample preparation and characterization of degraded CCLs are required in order to correctly identify the relevant phases with sufficient resolution. The objective of the present work is to gain an essential understanding of the state of Pt, carbon, and ionomer with greater spatial resolution in pristine and degraded CCLs without introducing any artefacts associated with conventional approaches. The existing gap in the literature on the degraded structure of porous electrodes is addressed by high resolution imaging of its components at the mesoscopic scale,

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http://dx.doi.org/10.1016/j.elecom.2016.08.018
1388-2481/

in particular by giving more emphasis on the ionomer phase in pristine and degraded CCLs.

2. Experimental

Membrane electrode assemblies (MEAs) with CCL comprising of commercial 50:50 wt% Pt/C with graphitic carbon support of 180 m^2/g surface area (BET) and 23 wt% Nafion ionomer were subjected to a voltage cycling accelerated stress test (AST) having a square wave pattern with lower (LPL) and upper (UPL) potential limits of 0.6 and 1.3 V with 30 and 60 s duration, respectively. The AST was operated until 4700 cycles when MEA failure by low fuel cell performance was reached. Further details on the MEAs and the implemented AST can be found elsewhere [14]. Catalyst coated membrane (CCM) samples were extracted from conditioned beginning-of-test (BOT) and end-of-test (EOT) MEAs by carefully peeling off the gas diffusion layers, embedded in epoxy resin, sliced to thin films (~70–90 nm) using a Leica UC6 ultramicrotome, and collected on copper grids for imaging. The CCLs were analyzed using a Tecnai Osiris transmission electron microscope (TEM) with energy dispersive X-ray (EDX) capability from FEI operated at 200 keV.

3. Results and discussion

The present study aims to investigate the structural effects of voltage cycling with a relatively high UPL intended to induce CCL degradation similar to that observed during regular operation of automotive PEFCs. The mesoscopic changes of the heterogeneous CCL structure are investigated using bright field imaging, high-angle annular dark field (HAADF) imaging, and EDX mapping of Pt, C, and F present in the CCL. The results are complemented with Pt particle size, electrochemical active surface area (ECSA), and fuel cell performance diagnostics.

The obtained bright field TEM image of the BOT CCL in Fig. 1(a) reveals the uniform heterogeneous porous structure throughout the cross section of the pristine CCL, although the individual platinum, carbon, and ionomer phases are difficult to interrogate in this image. The corresponding bright field image of the EOT CCL (Fig. 1(b)) exhibits a considerably more non-uniform distribution of porous structure along with irregular void features which are not seen in the pristine material. The observed solid phase agglomerations could be due to platinum sintering and ionomer redistribution, while the voids could be due to carbon corrosion as a result of voltage cycling. It is found from the bright field images that the EOT CCL has undergone an average of 73% thinning which is primarily believed to occur due to carbon support corrosion [14]. The distinct dark platinum band observed in the adjacent membrane evidences dissolution of platinum from the CCL, migration into the membrane, and redeposition in the membrane [15,16].

As shown in Fig. 2, the HAADF imaging which is sensitive to higher atomic number material provides an improved illustration of the composite solid phase structure of the CCLs. The white particles in the BOT image (Fig. 2(a)) are believed to contain Pt which appears bright due to its strong electron scattering behavior. The BOT image indicates uniform distribution of fine solids and voids whereas the EOT image (Fig. 2(b)) exhibits visibly aggregated solid and void features that are larger than those observed at BOT. Moreover, the higher solid content observed at EOT suggests a densification of the CCL with the applied AST, which means that the overall loss of pore space exceeds the overall loss of solid phase during the degradation process. However, despite the enhanced solid/void contrast, it is still difficult to distinguish the platinum, carbon, and ionomer portions of the solid phase from the dark field images.

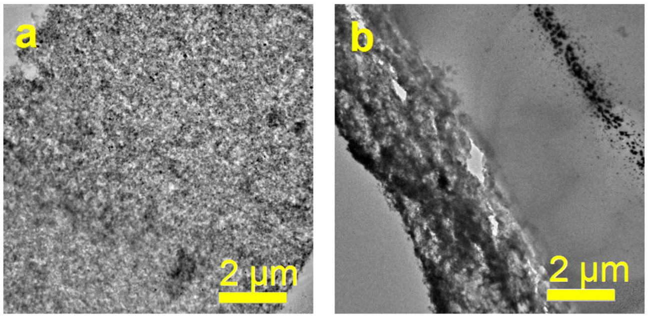

Fig. 1. Bright field TEM images of (a) BOT and (b) EOT cathode catalyst layers imaged at 2,300× magnification.

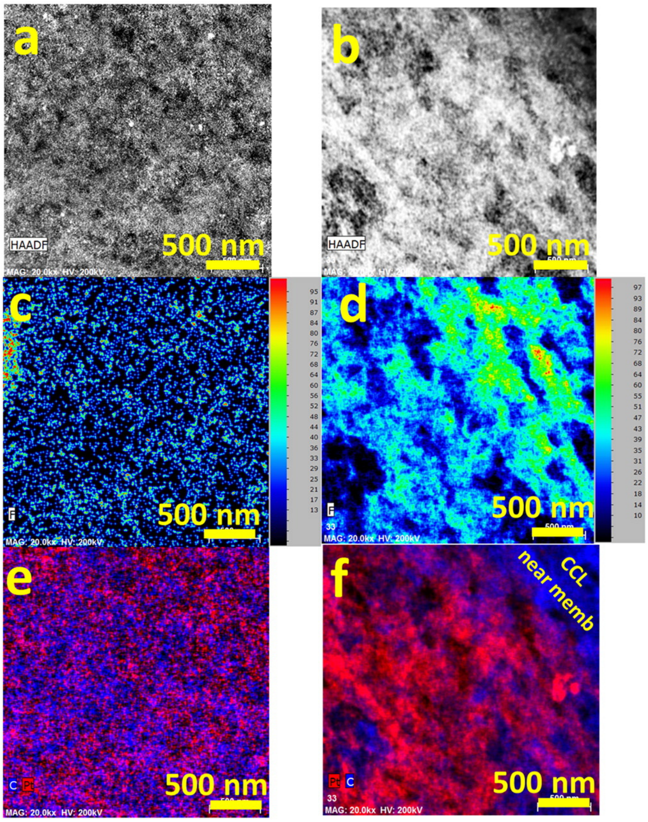

Fig. 2. Cross-sectional (a–b) high-angle annular dark field (HAADF) images, (c–d) fluorine maps (representing ionomer), and (e–f) carbon (blue) and platinum (red) maps for the (a, c, e) BOT and (b, d, f) EOT cathode catalyst layers. The GDL and membrane interfaces are located on the left and right sides, respectively, outside the field-of-view. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Since fluorine is the principal building block of Nafion ionomer while negligible elsewhere, the spatial distribution of ionomer phase is revealed quantitatively by the fluorine concentration maps in Fig. 2(c–d) obtained from EDX analysis. The BOT CCL results exhibit a homogeneously distributed fluorine concentration with a fine, thin film-like structure of high connectivity within the ionomer phase [11]. The fluorine concentration map of the EOT CCL, in contrast, reveals regions of non-uniformly distributed and large ionomer-rich features. Also, while high local gradients in fluorine concentration are regularly present at BOT, the EOT map is dominated by relatively large areas of low fluorine concentration gradient, comprising of separate regions of near-zero (void) and high overall fluorine concentration. The sparsely distributed fluorine across the entire BOT CCL cross section is not captured within the limited field-of-view of the map, whereas densely distributed fluorine across the thinned CCL is fully captured in the EOT image from the GDL side (left) to the membrane side (right). The increased ionomer content by the estimated fluorine at EOT is also confirmed through EDX spectral analysis. The redistribution of fluorine at EOT also implies large regions void of ionomer, which is evident from the micrograph in