Nanostructural characterization of catalyst layers in PEMFC: Sample preparation considerations

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The generation of electricity from renewable sources has gained a lot of attention due to its promise of reduced pollution and dependence on fossil fuel. The Proton-Exchange Membrane Fuel Cell (PEMFC) has gained increased interest from the scientific and commercial community for its application in automobiles and power generation plants [1]. The catalyst layers play an important role as they govern the rate of hydrogen oxidation and oxygen reduction taking place in the electrodes [2]. Platinum and potentially Pt-alloy nanoparticles are the most widely accepted catalysts for PEMFC. However, significant efforts are needed to understand the degradation mechanisms and the evolution of performance of the fuel cell [3, 4].

Characterization techniques such as Scanning Transmission Electron Microscopy (S-TEM) and Scanning Transmission X-ray Microscopy (STXM) are some of the most versatile and powerful tools that can be used to elucidate the structure, composition and chemical state of complex PEMFC components. Composition of single nanoparticles and alloying effects can be obtained with aberration-corrected TEM before and after electro-chemical testing [5]. STXM has also been used to study the Pt degradation and chemical state of PEMFC [4]. However, sample preparation for both S-TEM and STXM are important and crucial steps and detailed understanding of the nanoscale structure of samples prepared with different techniques needs to to be understood.

In this context, using TEM, S-TEM and STXM we have studied Pt based catalysts on carbon support in a cathode catalyst layer. The site-specific samples were thin lamellae prepared using a Focused Ion Beam (FIB) using Ga ions. This technique provides very effective preparation of samples for TEM analysis so that the composite structure is obtained (bright-field and dark-field TEM imaging, figure 1). With such samples it is thus possible to ultimately retrieve a faithful 3D-representation of the network using electron tomography. Analysis with high-angle annular dark-field HAADF imaging in STEM (figure 2), a technique sensitive to the atomic number, also shows very effectively the Pt distribution. However, detailed analysis in HAADF and x-ray microanalysis of the support material also demonstrates that some of the edges of the carbon black can contain significant contamination from the Ga source from the FIB (spectrum "1" in figure 3). This Ga presence is not uniform as demonstrated directly from HAADF imaging (Figure 2) but is also overlapping with the Pt particles (spectrum "2" in figure 3). Detailed comparison of TEM and STXM results helps understand the distribution of this Ga implantation, as well as other FIB artifacts, such as loss of ionomer component. Electron tomography will be used to render the full 3D structure and evaluate the localization of Ga and its role in the chemistry of the studied structure.

References
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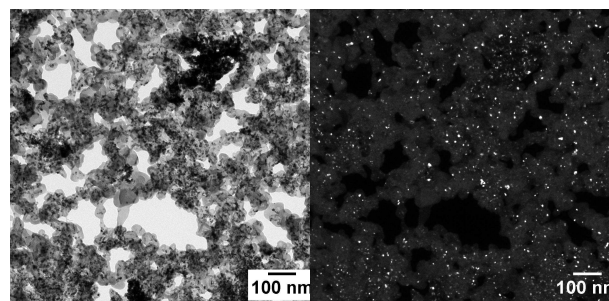[5] M.C.Y. Chan, et al, *Nanoscale*, **2012**, 4, 7273-79.

FIG. 1 Pt based catalyst coated membrane showing BF and DF images of a FIB-prepared sample of PEMFC.
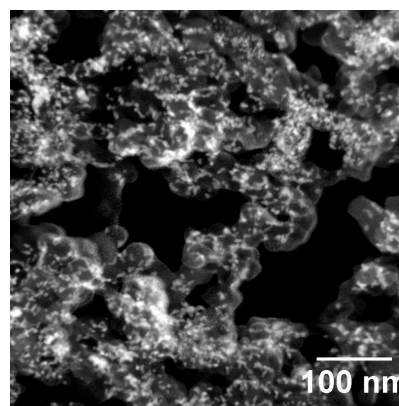

FIG. 2 HAADF image of Pt based catalyst on carbon support in a cathode catalyst layer showing Pt distribution on the carbon support.
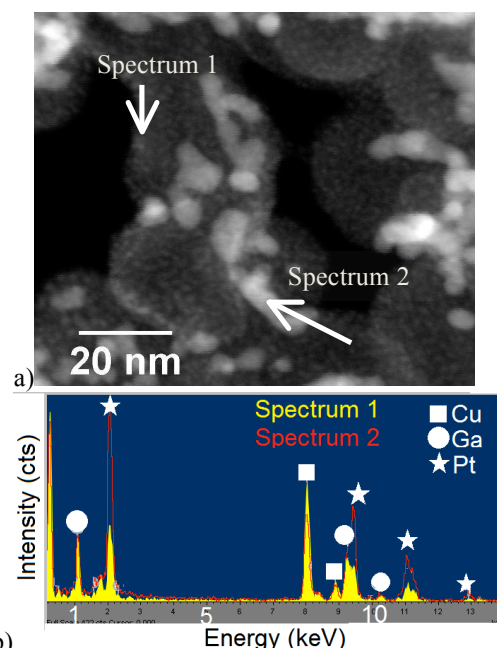

FIG. 3 a) HAADF image of the same sample as figure 2 b) EDX spectra from two different regions as shown in a), indicating composition of Pt and Ga.