A Novel Technique to Investigate Ionomer Distribution in PEMFC: Differentiating Carbon by STEM-EELS

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Proton Exchange Membrane Fuel Cell (PEMFCs) are promising energy conversion devices due to their high energy density, low operating temperature and high efficiency. The oxygen reduction reaction (ORR) in the electrode is strongly related with the ionomer/ carbon interface in the electrode. Thus, it is important to determine the ionomer coverage and location in the electrode.

In this context, Aberration Corrected-Scanning Transmission Electron Microscope (ac-STEM) coupled with Electron Energy Loss Spectroscopy (EELS) is a powerful tool to provide direct observations on the ionomer coverage/location in the electrode. Most of the previous research has focused on the presence of fluorine, which is a distinct element in the perfluorosulfonated ionomer, to be able to identify the ionomer/carbon interface by using energy dispersive spectroscopy(EDS). However, significant fluorine loss under electron beam has been also reported [1].

In this work, EELS analysis of Vulcan XC72 (carbon) and Nafion (ionomer) is employed to distinguish between these two kinds of amorphous carbon in the electrode of PEMFC. Single spectrum of both Vulcan XC72 and Nafion, under low electron dose of 2500e/A^2, is obtained in ac-STEM, after background removal and Fourier-ratio deconvolution. Comparison of the carbon K-edge in Nafion and Vulcan XC72 showed that the ratio of intensities between π*edge (at ~287ev) and σ* edge (~295ev) is different, as well as the energy loss near edge structure (ELNES). Moreover, an extra peak at ~292ev is shown in the spectrum of Nafion, which is primarily attributed to the carbonyl group in Nafion.

Spectrum images on the electrodes are obtained under the same condition for obtaining single spectrums for Nafion and Vulcan XC72. Principal component analysis (PCA) and multiple linear least square (MLLS) fitting is then applied to electrode spectrum images. The nafion and carbon distribution is clearly observed and easily distinguished. Meanwhile, the spectrum images of the electrode from the fluorine K-edge is also obtained, which shows good agreement with the results from the carbon K-edge but with a lower signal-to-noise ratio.

In summary, STEM-EELS characterization of the carbon K-edge provides a novel method to determine the interplay between the ionomer/carbon distribution on the electrodes of PEMFCs. As the cross section for carbon K-edge is normally higher than F-edge in EELS, this new method also provides insight into detecting low perfluorosulfonated ionomer contents in the PEMFCs.

Reference:

[1] D A Cullen, R Koestner, R S Kukreja, Z Y Liu, S Minko, O Trotsenko, A Tokarev, L Guetaz, H M Meyer III, C M Parish, K L More, J. Electrochem Soc 161, F1111 (2014)