Probing Interfaces in Fuel Cell Electrodes by XPS and HAXPES

Overview

Fuel cells are one of the fastest-growing alternative energy sources and the most promising technologies for market penetration in automotive applications and different consumer areas. Fuel cells consist of an anode, a cathode, and an electrolyte that allows either positively-charged hydrogen ions or negatively-charged hydroxyls to move between the two sides of the fuel cell. The catalyst layers on the anode and cathode consists of the catalyst material and ionomer, which provides ionic conductivity. The chemistry of the catalyst layer has the most significant impact on overall fuel cell performance.

Efforts to replace Pt-based oxygen reduction reaction (ORR) electrocatalysts with platinum-group metal (PGM) PGM-free alternatives, particularly transition metal–nitrogen– carbon (MNC) electrocatalysts, have advanced significantly. In MNC electrodes, the distribution of active sites that facilitate the oxygen reduction reaction, in "morphology of the ionomer" and structure of ionomer-catalyst interface within the cathode catalyst layers is critical. As shown in Figure 1, in the cathode catalyst layer, the catalyst is mixed with the ionomer Nafion, which interacts with the chemical groups on the catalyst's surface. Nitrogen chemistry is central to understanding the types and abundance of active sites present within the electrode, while carbon chemistry captures ionomer (Nafion)-catalyst morphology within the catalyst layer.

The application of XPS to study catalyst layers and their structure has become a standard analytical approach due to its chemical specificity, rich qualitative and quantitative information, and ease of access. While surface sensitivity of XPS is an important attribute, in some cases, the depth of analysis of XPS is not sufficient to analyze deeper gradients and interfaces without first sputter etching the sample surface. An alternative to sputter-etching the sample is Hard X-ray Photoelectron Spectroscopy (HAXPES), in which high energy hard X-rays (energy > 5kV) are used to provide a signal from depths of analysis three or more times than that of soft X-rays used on conventional XPS systems.

This note describes an application of a laboratory-based instrument, the PHI Quantes, equipped with two scanning microprobe monochromated X-ray sources, Al Kα (1486.6 eV) and Cr Kα (5414.8 eV), to fuel cell electrodes, thus enabling both traditional XPS and HAXPES experiments in the same instrument. Combining both soft and hard X-ray analyses, we can better understand the composition and structure at the surface and buried interfaces.
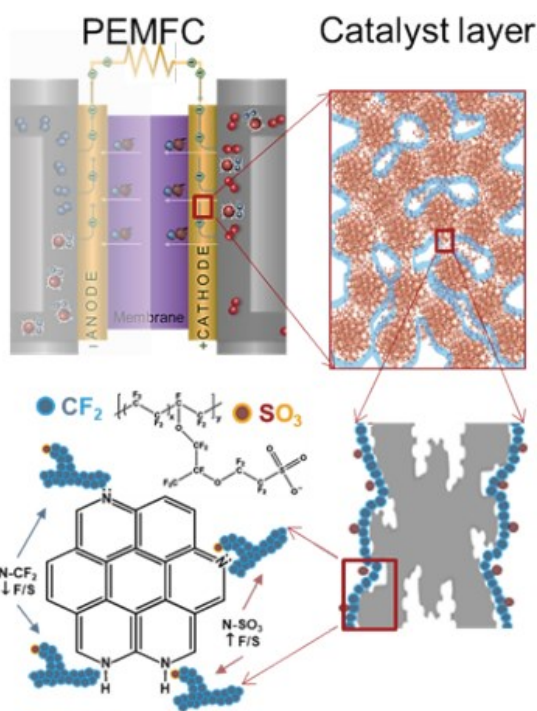
Figure 1. MNC catalyst layer structure

Figure 3 shows high-resolution N 1s and C 1s spectra obtained using Al and Cr X-ray sources. Cr probes 3x deeper into the electrode than Al source, providing essential information on species' enrichment at the surface. These species are responsible for both the kinetics of the (ORR) and water (which is a product of ORR) management. The surface is enriched in hydrogenated nitrogen (N-H) moieties, while there is more protonated nitrogen (N+) in the deeper layers. This is important as hydrogenated and protonated nitrogens have a different affinity toward oxygen-binding which is the first step of ORR. From the comparison of C1s spectra obtained at two different sampling depths, it is evident that the surface is enriched in ionomer while bulk has a larger signal from the catalyst itself.

The BIB consists of a broad Ar+ ion beam (of the order of 500mm diameter) with an energy of a few kV, attached to a vacuum chamber into which the sample is loaded. The voltage and intensity (current) of the beam can be varied to suit the application. The instrument may be used for improving an already mechanically polished surface using oblique irradiation just a few degrees above the sample surface, typically referred to as flat-milling, as shown in Fig 2a. Or it may be utilized to directly cross-section a material using a hard metal mask to create a milling edge whereby material under the mask is protected and material protruding from the mask edge is uniformly removed, as shown in Fig 2b. It is this second approach which is especially useful for LiB materials as they usually cannot withstand prior embedding and mechanical polishing.

Results

A unique feature of all PHI XPS instruments is a scanning micro-probe X-ray source which has probe size as small as sub-10 microns and as large as 300 microns. Using the smallest X-ray beam, it is also possible to generate X-ray induced secondary electron images (SXIs) that can be used for precise navigation and 100% accurate analysis area selection. Large area SXIs can be obtained using the mosaic option of the software from practically any size area selected on the sample. Figure 2 shows ~5 x ~5 mm stitched SXI images showing significant surface heterogeneity due to surface topography.

The very top layer of the electrode is ionomer-rich, as seen from Figure 3. In addition to its composition, it is also essential to understand the thickness of this layer as this layer is exposed to reactants, and thicker layers may block access of oxygen to buried active sites. XPS is too surface sensitive to probe this top layer entirely, while HAXPES provides a signal from both the very top surface layer and the deeper catalyst layer. The thickness of the ionomer-rich layer on top of the catalyst was calculated using the PHI StrataPHI algorithm for thin-film structures. Normalized peak intensities from single spectral acquisitions at 45° TOA were used to calculate thickness on the order of 25 nm (Figure 4) which is not accessible by soft X-ray analysis.
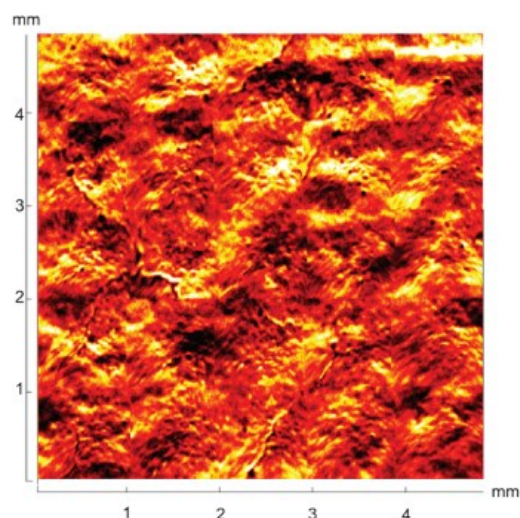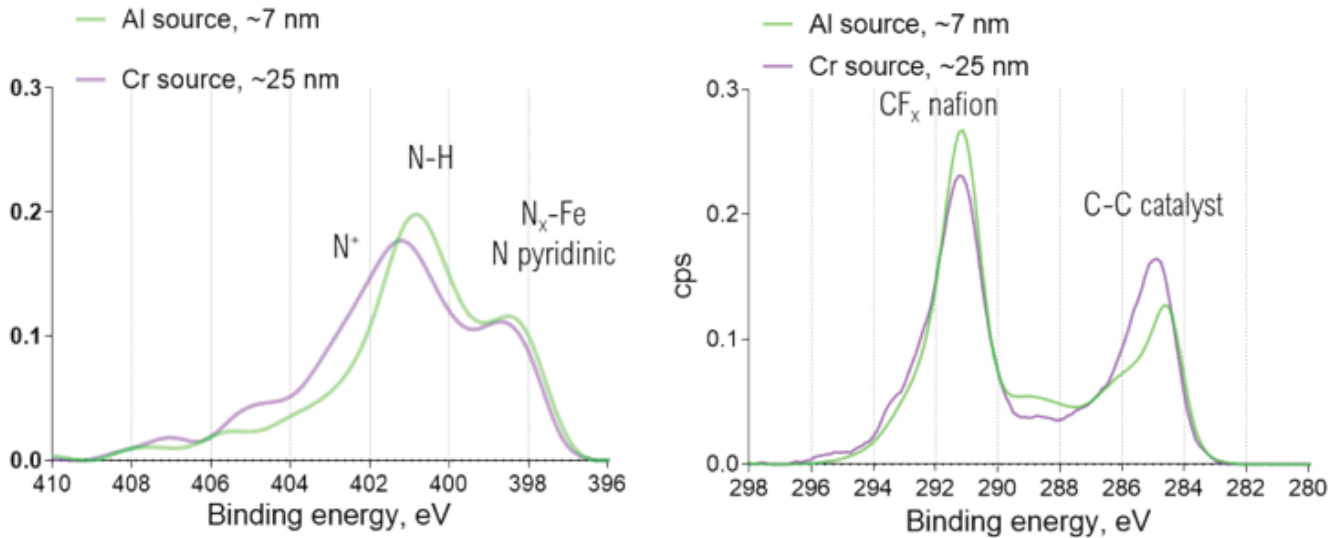

Figure 2. Large area SXI mosaic

Figure 3. Normalized N1s (left) and C1s (right) spectra acquired using Al and Cr sources from the same area on the electrode surface.

Gas Cluster Ion Beam (GCIB) is optimal for XPS depth profiling through organic structures such as polymers. We have used a 20kV cluster 2500 GCIB ion gun to remove the top layer of the ionomer to probe the chemistry beneath it. The sputter rate for this setting of GCIB is 54 nm per minute as determined for PMMA. After one minute of cleaning, most F and S from the ionomer is being removed, which is confirmed by a significant decrease of the CF2 peak from Nafion in the C1s spectrum. Important changes in N chemistry are detected as well. The surface-facing groups such as hydrogenated nitrogen are being removed to expose deeper active sites such as pyridinic nitrogen and nitrogen coordinated to iron.
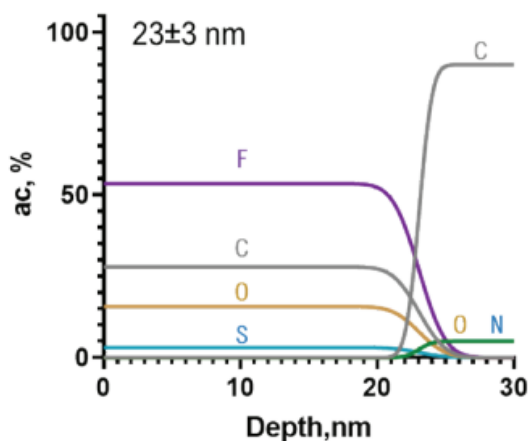

Figure 4. Structural analysis of ionomer/catalyst layer interface obtained from StrataPHI model of spectra HAXPES data!

Conclusion

PHI Quantes instrument offers a suite of solutions for studying interfaces of fuel cell electrodes – such as same area XPS and HAXPES, thickness calculations, and depth profiling using Gas Cluster Ion Beam.
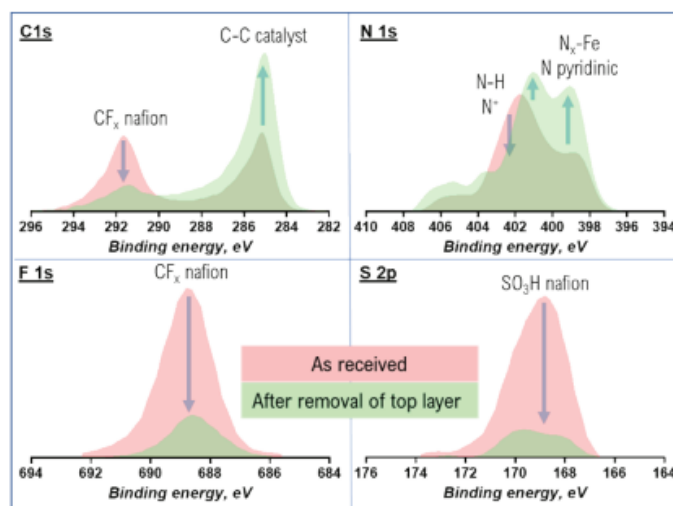

Figure 5. High-resolution C1s, N1s, f1s, and S 2p data for as received top electrode layer and after 1-minute sputtering using GCIB

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