

**Structural Correlations:
Design Levers for Performance and Durability
of Catalyst Layers**

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Durability of the catalyst layer (CL) is of vital importance in the large-scale deployment of PEMFCs. CL degradation is linked to catalyst dissolution and agglomeration, ionomer degradation, carbon support degradation, and the degradation of pore morphology and surface properties. It is essential to determine parameters representing composition, structure and properties of cathode components and catalysts layer for the optimization of performance and durability.

The structure, morphology and surface species of the catalyst powder will affect the ionomer and catalyst interaction and dispersion in the catalyst layers and therefore the catalyst layer morphology and chemistry. These, in turn, will affect the catalyst layer effective properties such as thickness, porosity, tortuosity, diffusivity, conductivity, etc. More specifically, the Nafion morphology in the catalyst layer will depend on the surface species of the catalyst powder. In this study, X-ray Photoelectron Spectroscopy (XPS) is used to quantify the surface species in MEAs tested under different accelerated stress test (AST) conditions. Figure 1 shows C 1s spectra for fresh and AST tested (4700 cycles, 0.6V for 30s to 1.2V for 60s) Pt50LSAC CCM samples.

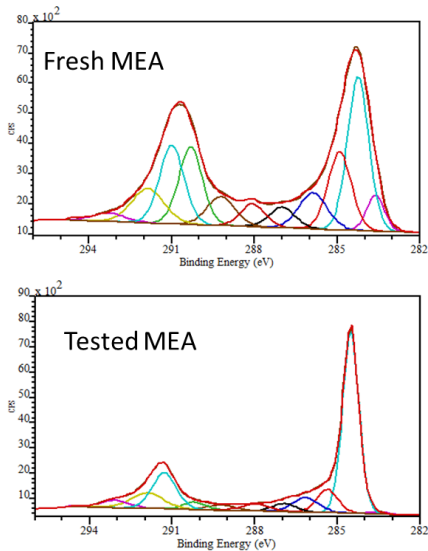


Fig. 1: High resolution C 1s spectra for fresh and AST tested MEA

C 1s spectra provide relative information of CF₂ and C-F species, which can be used to distinguish types of Nafion morphology in the catalyst layer. CF₂ is mainly present in the main chain while C-F is part of the side chains of the ionomer. As the carbon support becomes more functionalized (with more C_x-O_y groups), the CF₂:C-F ratio was found to decrease pointing to the enrichment of C-F side chains facing the pore. Conditioning (i.e. humidification) causes the ionomer to swell which results in changes of the ionomer morphology. For non-run MEAs, it

was observed that side chains prefer to interact with the surface functional groups of the carbon support (more CF₂ is detected), while for conditioned (humidified) MEAs, the ionomer hydrophilic side chains prefer to interact with the water in humidified pore (more C-F is present).

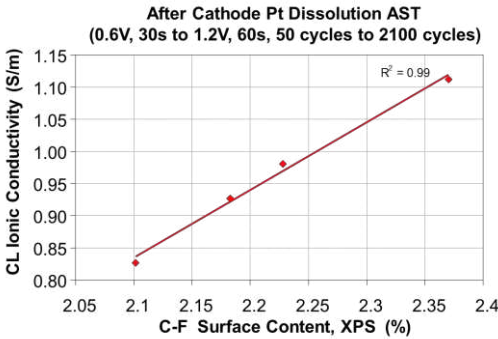


Fig. 2: CL ionic conductivity as a function of surface composition, C-F % as determined by XPS

Thus, the changes in surface C-F and CF₂ content with the operation and also AST cycling suggest an ionomer rearrangement. Figure 2 shows a correlation between CL ionic conductivity and the content of C-F side chain surface species. As with conditioning, AST cycling causes rearrangement of the ionomer i.e. more of C-F side chains, facing the pores rather than carbon support, get exposed. This allows water channels to form on the pore surfaces, facilitating proton transport and increasing ionic conductivity.

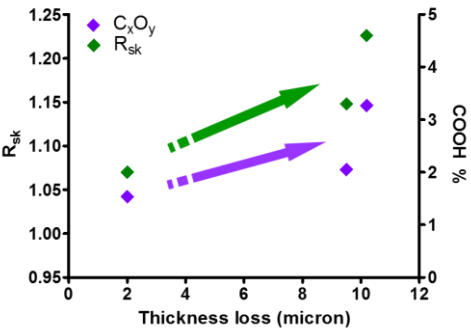


Fig.

3: Surface porosity and amount of carboxyl surface groups is correlated with thickness loss

Surface morphology is considered a key factor affecting the functional performance of MEA components. In order to understand changes in morphological properties of CCMs due to degradation, digital image processing of SEM images was performed. Figure 3 plots thickness loss that results during corrosion of carbon as a function of the amount of carboxyl groups and skewness R_{sk}. The skewness (R_{sk}) factor points to the domination of pores or peaks in the image reflecting the number of surface pores. With corrosion, carbon becomes more oxidized with a larger amount of surface oxides, as well as the larger number of pores due to the loss of carbon.

Correlations between composition, structure and properties of cathode components and the catalyst layer have been developed and linked to catalyst layer performance losses. The key interactions between materials properties and structure, catalyst layer effective properties, performance and durability, will provide design and optimization levers for designing MEAs for different operating regimes.

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