

Structure-Property-Performance Correlations - Towards Rational Catalyst Layer Design

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Proton exchange membrane (PEM) fuel cells are being developed as alternative energy sources for both residential and automotive application. In order for this technology to become fully commercial, the reduction of cost and improvements in performance and durability of PEM fuel cells membrane electrode assemblies (MEAs) are still required [1,2].

To address the requirement for further cost reduction the Pt loading of the cathode catalyst layer (CCL) needs to be reduced to 0.2- 0.1 mg/cm² while maintaining high currents and efficiency. Consequently, it becomes increasingly important to not only develop new catalyst materials, but also optimize the 3D structural arrangement of the CCL components such as catalyst, ionomer and void space so that all critical functionalities can be achieved simultaneously. In general terms this entails to provide sites catalytically active for ORR, and to further provide transport to/from these sites for the reactants O₂, protons, electrons and products H₂O and heat, respectively. Whereas tremendous progress has been achieved over the years using traditional ink based manufacturing methods [3] in reducing Pt loadings, the performance after ohmic correction at high current density shows a significantly larger decrease as the Pt loading approaches 0.1 mg/cm² than would be expected from a simple Tafel slope scaling due to the reduction in exchange current density. This "loading effect" has been observed by several authors [5] with explanations ranging from the oxide state of the Pt surface [6] to unknown transport losses at or near the Pt surface. Ohma et al. have proposed a transmission line model of CCL mass transport resistances distributed in through plane (z) direction with the Knudsen/ionomer diffusion resistances in series/parallel, respectively. This model could explain the loading effect if the ionomer diffusion resistance dominates mass transport in the CCL [7]. One question arising from these results is if the loading effect could somehow be associated with the structure of the CCL and if there are alternative CCL structures that do not suffer from such limitations.

The only alternative catalyst layer structures available on commercial scale are the so called nano-structured thin film (NSTF) catalyst layers available from 3M [4]. M. K. Debe has recently proposed a model based on kinetic gas theory where the collision frequency of gas molecules with the catalyst surface taking place in the Knudsen regime (i.e. assuming a gas phase process as rate determining) explains another effect, i.e. the differences of >1 order of magnitude in specific activities [mA/cm²Pt] observed between NSTF and traditional dispersed carbon supported catalysts [8]. According to the model, the high specific activities observed with NSTF are due to a structural effect, however, the loading effect is still observed albeit to a reduced extent compared to traditional CCL structures.

Therefore, in order to be able to design CCL

structures that meet the performance and durability requirements, it is necessary to obtain a better understanding of structure versus performance relationships. This requires the capability to fabricate different CCL structures, to characterize the spatial distribution of all components within the catalyst layer (carbon, Pt, ionomer and void), to measure the physico-chemical properties (both ex-situ and in-situ) and finally to use these experimental data as inputs for the development a model based understanding of the relationship between CCL structure and CCL performance and durability.

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