# New Approach to High-Efficiency Non-PGM Catalysts Using Rationally Designed Porous Organic Polymers

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Finding inexpensive and stable replacements for the platinum group metals (PGMs) has been the ultimate goal for proton exchange membrane fuel cell (PEMFC) catalyst research. Since the electrode/catalyst materials contribute to nearly half of a fuel cell stack cost, there is an urgent need to reduce or replace PGM usage. Among all the non-PGM candidates explored so far, transition metal doped nitrogen-carbon (TM-N-C) composites appear to be the most promising ones in promoting oxygen reduction reaction (ORR) at cathode [1-3]. Generally, these materials are prepared by forming TM-$N_4$ molecular or polymeric complex over amorphous carbon support, followed by thermal activation. Since non-PGM catalysts are known to have lower turn-over frequency *per catalytic site* when compared to platinum, their active site densities must be substantially higher to deliver a comparable performance. Using carbon support dilutes the active site density. Therefore, it is desirable to develop a catalyst preparation strategy that can circumvent the usage of the support and substantially increase the active site density with better ORR activity.

At Argonne National Laboratory, we developed recently several new synthesis approaches which significantly improved the activity of non-PGM catalysts in PEMFC. For example, we demonstrated that metal-organic framework (MOF) could serve as a new type of precursors to produce the "support-free" non-PGM electrode catalysts. [4] Different from the previous approaches, MOFs have the advantages of a clearly-defined 3-dimensional structure via transition metal-$N_4$ coordination, intrinsically high volumetric density of potential active site and high surface area and tunable pore sizes. More recently, we demonstrated that a binary MOF system, in which the ratio of two different transition metal contents can be varied, could achieve an even higher ORR performance. [5]

In this presentation, we will discuss a new approach to prepare high efficient non-PGM catalyst using porous organic polymers (POPs). POPs were recently emerged as a new type of materials for gas storage and separation. [7] When nitrogen-containing functionalities, such as porphyrin or phthalocyanine, are built into the porous network, this new material could be used to incorporate high density of metal ions with evenly distributed TM-$N_4$ in the network. We have applied this strategy to prepare a porous polymer with built-in Fe-$N_4$ structure through oxidative coupling of thiophene functionalized Fe-porphyrin monomers. The Fe-porphyrins constituted the pore walls of the network, and were subsequently converted into active catalytic sites for ORR through a thermal activation process. Figure 1 (inset) shows a schematic drawing of a three-dimensional structure of the as-synthesized polymer Fe-polyporphyrin, (PFeTTPP). Upon thermolysis, an excellent performance in catalytic ORR was observed. Figure 1 shows the geometric and volumetric current densities obtained from a single PEM fuel cell test. Excellent performance was achieved.

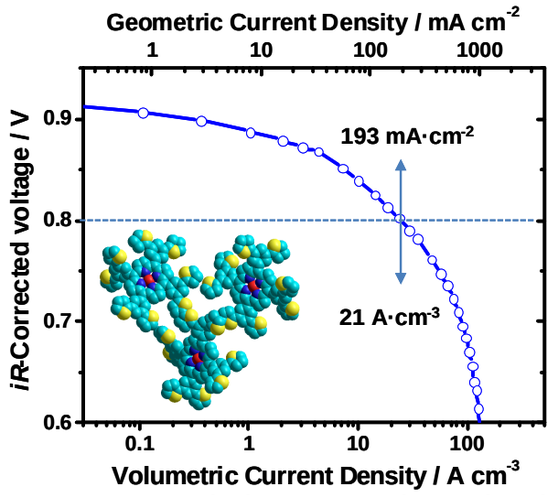


Figure 1. Geometric and volumetric current densities derived from a PEMFC single cell measurement using PFeTTPP based non-PGM catalytic cathode, fully humidified oxygen and hydrogen at 1.5 bar, Nafion 117. Inset: 3-D stack structure of PFeTTPP

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