

## Influence of ionomer/carbon ratio on porosity distribution, surface area and roughness of PEMFC catalyst layers fabricated by a direct dry deposition method

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Proton exchange membrane fuel cells (PEMFC) are poised for market penetration in the automobile, portable and back-up power markets. Cost and durability issues are crucial to the performance of PEMFC, which primarily depends on the design of catalyst layers [1]. Current catalysts layers use Pt supported on high surface area carbons (*e.g.*, Ketjen Black EC300-J and Vulcan XC-72R) with perfluorosulfonic acid (PFSA) ionomer as a binding agent. It is widely believed that incorporation of ionomer can extend the reaction zone, increase proton conductivity, and catalyst utilization [2].

The catalyst layers are predominately comprised of primary carbon particles, 20-50 nm in diameter, that then form secondary particles due to agglomeration and aggregation [3]. Stacking of these aggregates creates a unique 3D structure between the fractal structured carbon branches. Additional micropores (<2 nm) exist on the surface of the carbon. Catalyzing the carbon with Pt nanoparticles can block these micropores since the size of the Pt particles ranges between 2-4 nm.

Ionomer is distributed on the surface of carbon agglomerates and covers intra-agglomerate pores (<20nm) at lower ionomer content [4]. At higher ionomer content, significant blocking of the pores is observed which interferes with efficient water and gas transport. It is necessary to create an ionomer network with sufficient proton conduction that leaves pore space for water and gas transport [2,4]. The optimal ionomer content has been found to be around 30 wt% for ink sprayed catalyst layers [4]. It is also proposed that for anode catalyst layers, high ionomer content with a broader pore size distribution is advantageous for sorption and retention of water, whereas for cathode layers, lower ionomer content with a narrow pore size distribution would facilitate water removal which is beneficial for the oxygen reduction reaction [2,4].

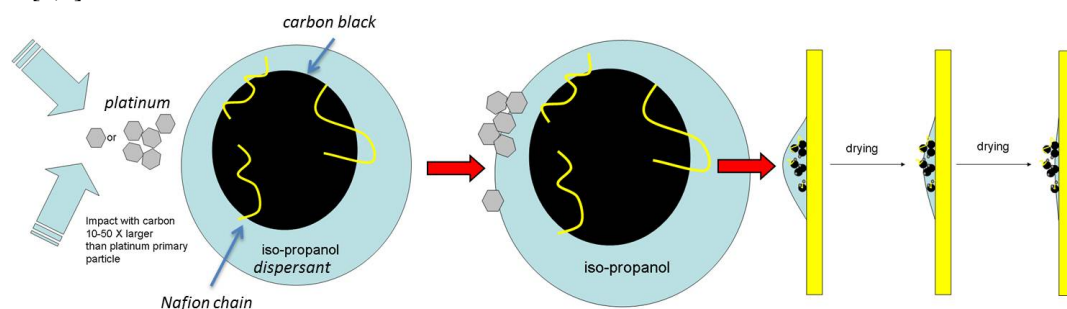


Figure 1: Schematic representation of catalyst formation and deposition by RSDT

The Reactive Spray Deposition Technique (RSDT) is a one-step, open-atmosphere and dry deposition method for applying PEMFC catalyst layers [5]. RSDT is able to make thin porous catalyst films with reduced platinum loading. In this process, platinum 2,4-pentanedionate is dissolved in xylene and liquefied propane and combusted through an atomizing nozzle. The droplets then burn through the flame resulting in metallic Pt nanoparticle formation. These Pt nanoparticles can homogeneously nucleate during time-of-flight or heterogeneously onto the carbon support as shown in Figure 1. The carbon and ionomer is sprayed, as a slurry, radially into the post combustion zone by secondary nozzles. Catalyzation of the carbon-ionomer composite occurs in-flight. Catalyst layer growth occurs via ballistic impact and sticks on a cast Nafion membrane.

The RSDT process generates uniquely structured catalyst layers that are very different from conventional techniques. Conventional methods spray or tape cast a pre-catalyzed support and ionomer slurry. The RSDT process essentially combines catalyst synthesis, film formation, and support catalyzation into one step. This unique method for building up the catalyst layer requires a better understanding of the pore forming network. Our work characterizes the porosity of catalyst layers using the Brunauer-Emmett-Teller (BET) model and Mercury Intrusion Porosimetry (MIP) and further investigates the influence of the ionomer/carbon ratio on this microstructure. The combination of BET and MIP covers pore size distribution over a wide range because BET measures pore size from 2 to 400nm while MIP measures 3 to 360 microns [3]. The ionomer/carbon ratios, for examination, are chosen from 0.16, 0.25, 0.5, 0.8, 1.0 to 1.2. The Pt/Vulcan carbon catalyst layer is directly deposited on Nafion 211 films. Micro- and macropore distributions are explored and compared to surface morphology and roughness characterized by scanning electron microscopy (SEM) and atomic force microscopy (AFM). Our goal is to determine an optimum ionomer/carbon ratio suited to the unique catalyst layers formation of the RSDT process.

### References:

- [1] Wang, Y., et al. Applied Energy(2011), 88, 981-1007.
- [2] Soboleva, T., et al. Applied Materials & Interfaces, 2011, 3, 1827-1837.
- [3] Yu, Z., et al. Fuel Cells, 2012, 12, 557-565.
- [4] Soboleva, T., et al. Applied Materials & Interfaces, 2010, 2, 375-384.
- [5] Roller, J., et al. Journal of Material Science, 2012, 47, 4604-4611.