



Review article

The catalyst layer and its dimensionality – A look into its ingredients and how to characterize their effects



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HIGHLIGHTS

- A review of catalyst layer ink ingredients is given.
- Ionomer as a binder and its effect are discussed.
- Alternative supports to the traditional carbon are discussed.
- Alloyed Pt catalysts and Pt-free catalysts are discussed.
- Characterization techniques are listed.

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ABSTRACT

Development of polymer electrolyte membrane (PEM) fuel cells throughout the years is established through its component optimization. This is especially true of its catalyst layer, where structuring of the layer has led to many breakthroughs. The catalyst layer acts as the heart of the cell, where it controls the half-cell reactions and their products. The complex nature of various transport phenomena simultaneously taking place in the layer requires the layer to be heterogeneous in structure. Hence, a delicate balance of the layer's ingredients, coupled with the understanding of the ingredients' interaction, is required. State-of-the-art catalyst layers are composed of a catalyst, its support, a solvent and a binder. Changes in the morphology, structure or material of any of these components ultimately affects the layer's activity and durability. In this review paper, we provide an overview of the various works tailored to understand how each component in the catalyst's ink affects the stability and life-time of the layer.

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1. Introduction

Advancement in polymer electrolyte membrane (PEM) fuel cells, specifically for automotive applications, has been achieved through systematic optimization of its components. The use of thinner components, specifically the membrane, and the use of structured catalyst layers are two of the main breakthroughs in this advancement. The importance of the catalyst layer to PEM fuel cells is dictated by its functions and its location between the porous transport layer (PTL) and the electrolyte membrane. As the area where the electrochemical half-cell reactions occur, it must provide continuous pathways for various species; primarily, (i) a continuous path for efficient transport of protons, (ii) continuous pore network for the transport of reactants/products and for efficient

water removal and (iii) continuous passage for the conduction of electrons between the catalyst layer and the current collector. In turn, the catalyst layer's structure is heterogeneous and complex and its optimization is required for the increase of its activity and the performance of the cell. This is further complicated by the requirement for its stability and durability over the lifetime of the cell and under various operating conditions.

The interconnection between structure optimization and the increase in power density of the cell is highlighted through the history of catalyst layer preparation. Methods for preparing conventional catalyst layers date back to 1967, when Niedrach [1] used polytetrafluoroethylene (PTFE) as the binder to hold fine powder metal catalyst particles together. However, proton conduction was lacking within these PTFE-bonded catalyst layers as Raistrick later showed [2]. Hence, a method of impregnating Nafion® solution through the surface of a finished catalyst layer was developed. This was a breakthrough in which it highlighted the importance of a 3-

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phase interface. Brushing a Nafion[®] solution on the electrode surface to introduce Nafion[®] within the catalyst layer was later developed by Ticianelli et al. [3]. Uchida et al. [4] utilized the colloidal method to mix a perfluorosulfonated ionomer directly with the catalyst powder; however, still used PTFE as the binder. The use of PTFE as the binder required high Pt loadings. The main breakthrough came when Wilson and Gottesfeld [5,6] eliminated the use of PTFE all together by using recast Nafion[®] ionomer as the binder and significantly reduced the amount of Pt loadings. Subsequently, Pt-black, i.e. unsupported Pt, was replaced with Pt supported on carbon to reduce the metal content. The structure of this state-of-the-art catalyst layer, Fig. 1(a), is typically formed by the dispersion of an ink comprising a catalyst deposited onto a support (e.g. Pt/C), binder (e.g. PFSA ionomer) and a dispersing solvent. The structure of the layer is, hence, shaped within the ink by the agglomeration of the carbon particles and the aggregation of the ionomer. The dispersion medium governs the ink's properties, such as aggregation size of the catalyst/ionomer particles, viscosity, rate of solidification and ultimately the physical and mass transport properties of the catalyst layer [8]. In this case, the binder material used in the preparation of the ink is required to be a proton conductor. Any imbalance in the amount of the ionomer in the catalyst layer can result in transport losses. Too little ionomer results in poor ionic conductivity and reduced active sites, while too much results in flooding of the layer and ultimately, slow diffusion of the gases to the reactant sites. Understanding how the ionomer distributes within the catalyst layer is important in optimization studies of the layer and there is great evidence in literature that points to the aggregation of the ionomer solution [8,9]. Durability and stability of the catalyst layer is hence governed by its catalyst utilization, rate of support degradation (e.g. carbon corrosion) and ionomer stability [10,11].

Efforts to increase the stability of the catalyst layer are always ongoing with some focused on increasing the durability of various components, such as the binder or the support and others on finding alternative preparation methods. The latter is achieved by looking at decreasing the catalyst layer's thickness by eliminating one or more of the ingredients mentioned earlier. An example of such efforts are catalyst layers fabricated by the dispersion of Pt on the gas diffusion layer or dispersion of Pt/C on the electrolyte membrane, forming a very thin layer between the PTL and the electrolyte membrane [12–14]. Another such example are ultra-thin catalyst layers (UTCL) or nano-structured thin film (NSTF) catalyst layers. These catalyst layers are ionomer-free and are often composed of nanostructured support, such as gold or carbon, on which the catalyst is dispersed. The 3 M thin film catalyst layer, Fig. 1(b), is in the forefront of research and has shown high catalytic activity and very high stability and durability. The catalyst is supported on thin whiskers manufactured from an organic material, Perylene red 149, which does not take part in the transport phenomena within the layer. The 3 M catalyst layer contains neither carbon nor additional ionomer and thus, durability issues due to carbon corrosion and ionomer degradation are eliminated [11]. However, as discussed later in this paper, other issues with such a catalyst structure arise. Other efforts have been focused on fabricating structured catalyst layers. In Ref. [15], Zhang and Shi combined the benefits of using PTFE and ionomer as a binder in fabricating a dual-bonded catalyst layer. With using a structured catalyst layer using an ionomer-bonded and PTFE-bonded catalyst layer, they reported an improvement of about 25% in the electric yield rate. Dual-layer structured electrodes have also been investigated in Ref. [16], where the effect of varying PTFE content as well as layer thicknesses was examined. In Ref. [17], Su and co-workers structured the catalyst layer by fabricating a double catalyst layer

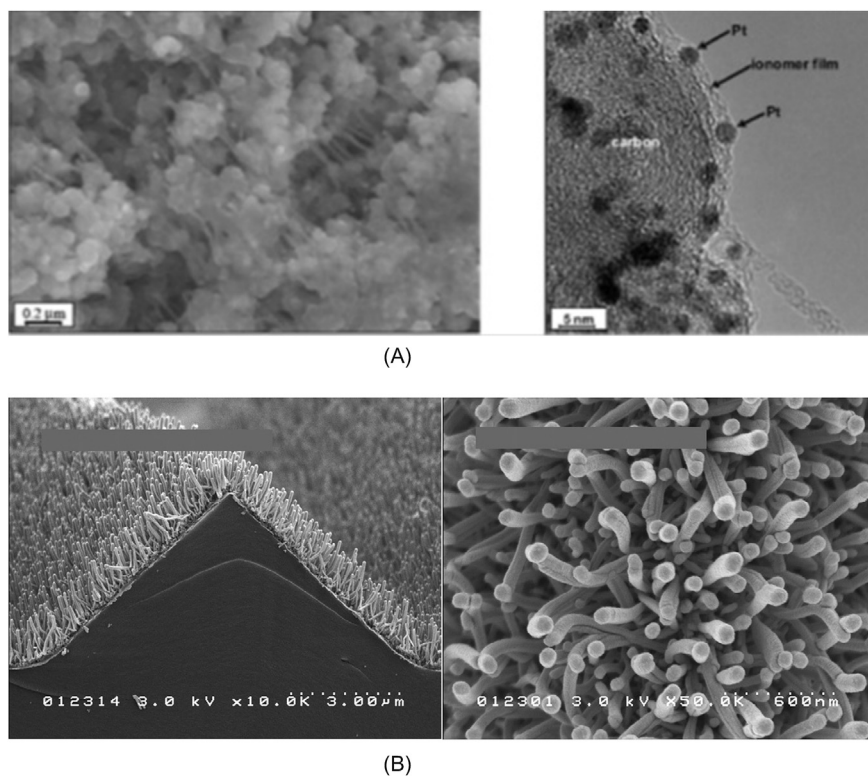


Fig. 1. (a) SEM (left) and TEM images (right) showing catalyst layer and ionomer strands that bind Pt/C agglomerates and an ionomer film, respectively [7] Reproduced from Ref. [7] with permission from the Electrochemical Society; (b) Scanning electron micrographs of typical NSTF catalysts as fabricated on a micro-structured catalyst transfer substrate, seen (left) in cross section with original magnification of X 10,000, and (right) in plane view with original magnification of X 50,000 Reproduced from Ref. [21] with permission from Elsevier.

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