



Full length article

Investigation of catalytic vs reactant transport effect of catalyst layers on proton exchange membrane fuel cell performance



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HIGHLIGHTS

- Evaluated catalytic (kinetic) vs mass diffusion effect on fuel cell performance.
- Better cell performance for catalyst layers with lower mass diffusion resistivity.
- Not necessarily better cell performance for better catalyst kinetic characteristics.
- Lower mass diffusion resistivity for catalyst layers made by spraying technique.
- Demonstrated the importance of diffusion effect, hence the catalyst layer structure.

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ABSTRACT

For proton exchange membrane fuel cells (PEMFC), the importance of catalytic (kinetic) effect is widely recognized with less attention being paid to mass transport (diffusion) effect. In this study, the importance of kinetic and diffusion effect on PEMFC performance is investigated experimentally by using different catalysts and catalyst layer (CL) fabrication methods of spraying and brush-painting, both of which are commonly used, simple and low-cost with volume-production capability. It is found that as a catalyst, 20% Pt/C has better kinetic characteristics than 60% Pt/C in terms of smaller Pt particle size, better Pt dispersion, less Pt agglomeration, and larger active surface area. For the same Pt loading, the porosity is almost identical for the CLs made of the two catalysts by the two fabrication methods, but the diffusion resistivity for the CLs made of 60% Pt/C is smaller than its counterpart for the CLs made of 20% Pt/C, due to difference in the effective diffusion coefficient and CL thickness. As a result, the performance of the PEMFC made of 60% Pt/C is better than the corresponding PEMFC made of 20% Pt/C. Similarly, for PEMFCs made of the same catalyst, the diffusion resistivity is smaller for CLs made by spraying compared with brush-painting method, leading to better performance for the PEMFC made by spraying method. These results highlight the importance of diffusion effect, hence the structure of the CLs, in determining the PEMFC performance.

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1. Introduction

Proton exchange membrane fuel cell (PEMFC) is a clean and efficient power source with high power density. Its low temperature operation allows fast startup, beneficial for mobile applications, but it necessitates the deployment of expensive platinum (Pt) catalyst to facilitate the electrochemical reaction for power generation. The catalyst is made into a thin layer, called catalyst layer, located in between the polymeric membrane and the gas diffusion layer (GDL). It is well known that cell performance is strongly affected by the type of catalyst, and the structure of the catalyst

layer (CL) through which reactant transports in for electrochemical reactions leading to power generation [1–5].

Since catalyzed electrochemical reactions occur on the surface of the expensive catalyst, and the catalyst surface area increases when the catalyst particle size is decreased for a given amount of catalyst used, catalyst particle sizes have been typically reduced to nanometers in order to reduce the catalyst loading for cost saving [6,7]. However, catalyst nanoparticles packed into the catalyst layer do not provide sufficient pore volume for the transport of reactant, mainly by diffusion mechanism, into the layer for electrochemical reaction. Therefore, they are supported on much larger meso-scale carbon particles (C), hence often referred to as Pt/C catalyst, to yield sufficient pore structure for reactant transport [8–10]. As a result, Pt to C ratio, and the size, dispersion and

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agglomeration of the Pt nanoparticles all have significant impact on fuel cell performance through the impact on the catalyzed electrochemical reactions [11,12], which is in general referred to as the kinetic effect. Numerous studies have been devoted to the development of more active catalysts for fuel cell application, and a comprehensive review is available for the critical roles of Pt/C catalysts and Pt to C ratios in fuel cell application [7,13].

The activity of 20%, 40% and 100% Pt-C (by weight) catalyst is compared through a half-cell experiment for the oxidation of ethanol by using the cyclic voltammetry (CV) results [14], suggesting higher activity and stability of 20% Pt/C catalyst than 40% and 100% catalyst. The effect of Pt to C ratio is investigated [15] for the surface morphology through TEM images, indicating a higher dispersion of Pt for catalysts with a lower Pt to C ratio; and for oxygen reduction reaction (ORR) activity through CV results, showing higher specific active area and mass activity again for catalysts with a lower Pt to C ratio as well; hence a better fuel cell performance is obtained for catalysts with a lower Pt to C ratio. Further studies regarding the PEMFC performance have been conducted with catalysts of different Pt to C ratios. For example, higher power density for 40% Pt/C catalyst is reported compared with 20% Pt/C catalyst, attributed to the higher porosity of the catalyst layers made of 40% Pt/C catalyst [16,17], and the highest maximum power density is achieved for 70% Pt/C catalyst among the four catalysts with 20%, 40%, 50% and 70% Pt to C ratio investigated [18].

On the other hand, the structure of the CL also plays a key role in the production of power because the reactant must be able to transport to the catalyst surface for reaction to occur, especially at high current density or high power density operations, which might be referred to as the diffusion effect, as reactant transport through the CL and the GDL to the reaction site is dominated by species diffusion. Despite the recognition or attribution of the importance of the porosity or structure of the CL [19,20] fewer studies have been devoted to in comparison with the number of studies dedicated to catalyst materials. Different methods have been employed to measure the porosity and pore size distribution of porous materials [21–24]. Standard Porosimetry (MSP) is capable of detecting a wide range of pore sizes (0.3 nm–300 μm), without any deformation of the samples, and is thus suitable for the pore structure characterization of the catalyst layer [25]. Perhaps, more important is the measurement of the effective diffusion coefficient, which represents the capability of the CL in the transport of reactant, and a number of experimental methods are available for the determination of diffusion coefficients [26,27]. Among these, one of the highly reliable methods is the closed-tube method, where the relative uncertainty for bulk diffusion coefficient measurement can be as low as 1–3% [28]. This method has been modified for the measurement of the effective diffusion coefficients of porous media, including the CLs [27,29]. It is recognized that the structure of the CLs made of the same catalyst may be influenced considerably by the method for catalyst deposition [28], and a variety of methods have been used, such as sputtering, doctor blading, chemical vapor deposition, inkjet printing, screen printing, etc.; however, these methods have a low adhesion and high catalyst waste, need expensive equipment with low deposition rate [30–36]. Spraying and brush-painting are two methods that are simple, cost-effective and have volume production capability, and hence widely used in practice [36–41], and will be used in the present study as well.

It is clear that despite its importance, few experimental studies have been directed to probe the impact of the porosity and reactant transport in the CL on the PEMFC performance. Therefore, the objective of the present study is to investigate the effect of both the Pt to C ratio and the CL structure in terms of the two important characterizing parameters of porosity and effective diffusion resistivity on the cell performance. The catalysts used will be analyzed

for its morphology and electrochemical activity, and CLs made by spraying and brush-painting techniques will be characterized by measuring the porosity and pore size distribution, as well as the effective diffusion coefficient. Then the CLs will be made into a single PEMFC, and its full cell performance will be measured as well. Two catalysts with Pt to C ratio of 20% and 60% will be used, and the importance of mass diffusion effect will be demonstrated in comparison with the kinetic effect of catalyst in terms of catalyst surface area and electrochemical activity.

2. Experimental

2.1. Materials

Nafion 211 and Nafion solution (5 wt%) are applied as membrane and ionomer, respectively. The catalyst used is Johnson Matthey HisPEC™ Fuel Cell Catalysts, 9100 with (55.5–58.8)% Pt to C ratio (nominally referred to as 60% Pt/C), and 5000 with (18.0–21.0)% Pt to C ratio (nominally referred to as 20% Pt/C) [42]. 2-Propanol (99.9% purity), and carbon paper (AvCarb with the thickness of $212.6 \pm 1.4 \mu\text{m}$ and the porosity of $72.8 \pm 0.5\%$) are used as the solvent, and gas diffusion layers (GDLs), respectively.

2.2. Ink preparation

The catalyst ink is prepared by dispersing the proper amount of the Pt/C catalyst, with 2-propanol, and Nafion solution. The weight ratio of catalyst to Nafion is set at 3:1, respectively. The prepared ink is sonicated for 1 h to reach a uniform suspension.

2.3. Catalyst layers and cell preparation

The CLs are very thin with weak mechanical strength, delicate to handle and are challenging to characterize, hence they are made based on the catalyst-coated substrate method (CCS). The prepared ink mixture is sprayed or brush-painted on GDLs, which is firstly placed on a vacuum table, at a temperature of 60 °C. The cathode and anode Pt loading are 0.4 and 0.1 mg/cm^2 , respectively. Membrane is then sandwiched between the catalyzed GDLs, followed by hot press process at 130 °C and 1000 psi for 3 min to form a single cell unit, which is often referred to as the membrane-electrode assembly (MEA). At this high total Pt loading of 0.5 mg/cm^2 , the MEA performance is almost identical for the MEAs made with different procedures, such as decal transfer method [43].

2.4. Porosity measurement of catalyzed electrodes

As mentioned earlier, the CLs are too weak to handle and be characterized alone. Therefore, they are made through CCS method by either spraying or brush-painting the prepared ink mixture on the GDL. Then the pore structure of the GDL and catalyzed GDL (i.e., GDL with the CL) are measured by using the Method of Standard Porosimetry (MSP), which was developed based on the capillary equilibrium [25,29]. The samples are cut into a disk-like shape with a diameter of 2.3 cm, and for each measurement, two pieces of samples are stacked and tested.

2.5. Effective diffusion coefficient measurement of catalyzed electrodes

The effective diffusion coefficient of the catalyzed and uncatalyzed GDLs is measured using a modified Loschmidt Cell, which is based on Fick's law of diffusion [44]. The Loschmidt Cell consists of two chambers, used to store the nitrogen and oxygen gases separately. Both gases are pure (99.99%). First, the bulk diffusion coefficient is measured without the CL samples placed between the

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