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Statistical prediction of fuel cell catalyst effectiveness: Quasi-random nano-structural analysis of carbon sphere-supported platinum catalysts

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ABSTRACT

In this study, a three-dimensional material network model is developed to visualize the nanoscale structures of carbon sphere-supported platinum (Pt/C) catalysts and to examine the effective transport paths to optimize the performance of randomly disordered, ternary-phase fuel cell catalysts. The catalyst layer domain is modeled using a quasi-random stochastic Monte Carlo-based method that utilizes random number generation processes. Successful interconnections of the three catalyst components are identified, and the catalyst effectiveness is defined to statistically estimate the fraction of the fuel cell catalysts that are utilized. Various fuel cell catalyst compositions are simulated to elucidate the effects of the electron, ion, and mass transport paths on the catalyst effectiveness. The statistical data show that at low ionomer contents, the accessible pore ratio is maximized, enhancing mass transport, and the effective ionomer configuration therefore significantly affects the catalyst effectiveness. In contrast, at high ionomer volume fractions, the ionomers form agglomerate chains that effectively transport ions, whereas the average accessible pore ratios are relatively low. More importantly, this study reveals that the maximum effectiveness depends strongly on the accessible pore ratio and the optimal ionomer volume fraction is inversely proportional to the Pt/C volume fraction.

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Introduction

In polymer electrolyte fuel cells (PEFCs), a set of thin porous components (i.e., gas diffusion media and catalyst layers) is compressed to enhance the heat, mass, and ion transfer [1,2]. These conventional catalyst layers (CLs) mostly consist of inhomogeneous, multifunctional, ternary-phase media with complex morphological structures. The three material phases

include ionomers, carbon-supported platinum catalysts, and pores, as shown in Fig. 1 [3]. The reactants and products diffuse through the pores in both the gas diffusion media (GDM) and the catalyst layers, and ions and electrons flow through the ionomers and carbon fibers, respectively [4,5]. The reactant, ion, and electron transport in and electrochemical kinetics of the fuel cell catalyst layers control their performance [6–8]. Both the facile reactant supply to the catalyst layers through the channels in the nano-porous media and the enhanced

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Nomenclature

A	area, m ²
E	catalyst effectiveness
f	probability density function
l	dimensionless distance from the GDM/CL interface (through-plane direction)
L	window length of a cube, m
n	total sample number
N	trial number
Pr	probability mass function
Pt/C	carbon sphere-supported Pt catalyst
r	areal accessible ratio
AR	accessible ratio
REV	representative elementary volume
V	volume, m ³
x	abscissa in the in-plane direction
y	ordinate in the in-plane direction
z	through-plane direction

Greek letters

α	rejection rate
ε	relative gradient error
δ	absolute difference between the estimated and expected mean volume fractions
μ	true mean of the random variable volume fraction
σ	true standard deviation of the random variable volume fraction
ϕ	volume fraction
φ	random variable volume fraction
Φ	cumulative normal distribution function

Superscripts

eff	effective value
k	component
cat	carbon sphere-supported Pt catalyst
io	ionomer
po	pore

Subscripts

i	sampling location index
m	incremental step index
n	trial number
REV	representative elementary volume

catalytic activity of noble metal catalysts strongly affect the electrochemical reactions and thus ultimately control the fuel cell performance [9–11]. Therefore, it is important to develop stochastic methods for modeling the spatially disordered nano-structure of fuel cell catalyst layers and for estimating the catalyst effectiveness to improve simulations of nanoscale fuel cell dynamics and to reduce the use of noble metal catalysts and the overall fuel cell cost.

Various methods have been employed to model the microscopic networks in catalyst layers and have revealed their complex hierarchical structures and electrochemical properties [12–20]. Wang et al. modeled catalyst layers using a simplified three-dimensional configuration and performed direct numerical simulations (DNSs) [12,13]. They randomly constructed the

catalyst layers from two components, such as mixed electrolyte/electronic and gas phases, to demonstrate the effects of the morphological parameters on the transport phenomena.

The carbon-supported catalyst in the electronic phase was assumed to be covered by a thin electrolyte film, through which the gas phase diffused. Similar to Wang et al., Suzuki et al. also assumed that the catalyst layer consisted of two components and used percolation theory to visualize the three-dimensional structures of carbon materials and electrolytes in PEFCs [14]. SEM (scanning electron microscopy) and TEM (transmission electron microscopy) images of the catalyst layer structure showed that the carbon materials formed agglomerated structures that were partially covered by the ionomer (electrolyte) phase [15,16]. Malek et al. utilized a coarse-grained molecular dynamics (CGMD) method to investigate the random, inhomogeneous ionomer structural configurations and the pore morphology that resulted from the self-organizing interactions between carbon black and the ionomer [17,18]. Thiele et al. reconstructed the three-dimensional pore structures of agglomerated carbon black cathode catalyst layers obtained by tomographic focused ion beam-scanning electron microscopy (FIB-SEM) to investigate the mass transport characteristics in the PEFC catalyst layer [19]. Litster et al. analyzed the morphologies, pore structures and transport characteristics of fuel cell electrodes using nanoscale X-ray computed tomography [20].

Fig. 1(b) shows a high-resolution SEM image of the nano-structure of a conventional carbon black-based catalyst layer. The SEM images in this work were provided by Drs. Taeyoung Kim and Young-Gi Yoon of Korea Institute of Energy Research (KIER) (Daejeon, Republic of Korea). In most commonly used carbon black-based catalyst layers, the catalysts are located not only on the agglomerated carbon particle surfaces but also within the agglomerates, where they are inaccessible to the reactants and ions, resulting in low catalyst utilization [11].

In contrast, carbon sphere-supported catalyst layers are a promising alternative [21]; several studies have reported that carbon sphere-supported catalyst layers have higher electrochemical surface areas, which improve the fuel cell performance [21–27]. Zhang et al. developed a method for synthesizing carbon spheres for PEFC applications and investigated the morphological structures of the cathode catalyst layers [22,23]. They confirmed that the gas diffusion and reaction surfaces can be increased considerably when carbon spheres are used as the catalyst support instead of carbon black. Yu et al. also reported that using carbon sphere catalyst supports can improve the fuel cell performance [24–26]. In their studies, the hierarchical carbon sphere nanostructures resulted in the formation of a widely interconnected pore network and higher electrochemical catalytic activity. Lange et al. developed a pore-scale model to simulate transport phenomena and the electrochemical reactions in carbon sphere-based catalyst layers and confirmed that the effective oxygen diffusivity increases with increasing carbon sphere diameter [27].

Fig. 1(c) shows a sample SEM image of a carbon sphere-based catalyst layer in a membrane electrode assembly (MEA). The detailed fabrication procedures of the carbon sphere-based catalyst layer and the SEM experiments were performed at Korea Institute of Energy Research (KIER). The

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