Electrochimica Acta 207 (2016) 187–197

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Integrated Statistical and Nano-Morphological Study of Effective Catalyst Utilization in Vertically Aligned Carbon Nanotube Catalyst Layers for Advanced Fuel Cell Applications

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ARTICLE INFO

Article history:
Received 25 January 2016
Received in revised form 28 April 2016
Accepted 30 April 2016
Available online 2 May 2016

Keywords:
polymer electrolyte fuel cells
vertically aligned carbon nanotubes
catalyst utilization
nano morphology
statistical analysis

ABSTRACT

In this study, a three-dimensional quasi-random nano-structural model based on the Monte Carlo method is proposed to evaluate effective catalyst utilization in fuel cell catalyst layers. Reflecting the intrinsically inhomogeneous nano-morphology of fuel cell catalyst layers, statistical analyses are performed to statistically compare various types of fuel cell electrodes to gain fundamental insight into the effects of morphological nano-structures on the catalyst utilization. For the detailed morphological analysis, a series of multi-component distributions at a 95% confidence level is randomly generated to deduce the statistical variations of the effective transport paths of ternary catalyst components. The statistical nano-morphology model is validated against published experimental data with good agreement. Subsequently, the morphological configuration of the vertically aligned carbon nanotube (VACNT) catalyst layers is simulated to determine the principal nano-design factors for improved catalyst utilization in the same stochastic manner which is used for carbon-supported catalyst layers. In the VACNT catalyst layers, all of the Pt/CNTs are successfully interconnected and therefore, all solid conducting carbon nanotubes can be utilized as electric current paths. Numerical results reveal that despite the relatively poor interconnections of the ion and mass transport paths, the statistical average catalyst utilization of VACNT is significantly improved when compared to conventional catalyst layers. It is also found that the ionic current paths of the VACNT catalyst layers can be considered as a catalyst utilization determining factor and an adequate amount of ionomers are necessary to promote successful ionic conduction. Finally, the average catalyst utilizations for both the regularly patterned in-line and staggered VACNT catalyst layers are compared with results for randomly distributed VACNTs.

1. INTRODUCTION

In polymer electrolyte fuel cell (PEFC) systems, feed stream gases react to generate electrochemical power in a thin compressed porous zone referred to as the catalyst layer (CL) [1]. Generally, these catalyst layers are fabricated by a catalyst ink-based process [2,3] and form mostly inhomogeneous micro-structures of ternary material phases: platinum/carbon (Pt/C) catalysts, ionomers, and pores. Intrinsically, catalyst layers are considered as a performance-determining component due to complex morphological structures that lead to both functional limitation of mass transport phenomena and underutilization of the Pt catalyst [1,4,5]. Therefore, it is of great importance to maximize the catalyst utilization to reduce the amount of noble catalyst and overall cost of fuel cells.

Numerous researches have focused on fabricating ultra-low Pt loading membrane electrode assemblies (MEAs) for PEMFCs and optimizing catalyst layer structures to improve transport phenomena and electrochemical kinetics [4–8]. Experimental studies have demonstrated complex hierarchical structures of catalyst layers and revealed the pore network characteristics of agglomerated carbon and ionomer structures [4,9–11]. Based on these experimental results, various modeling studies have suggested that the optimal composition of the catalyst layers can improve the ionic conductivity and mass transport, resulting in enhanced electrochemical reactions [12–18].

Wang et al. proposed a direct numerical simulation (DNS) model in order to demonstrate the effects of morphological parameters on transport phenomena [12,13]. In the DNS model, the catalyst layers were simplified by using binary components such as

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http://dx.doi.org/10.1016/j.electacta.2016.04.178
0013-4686/

an agglomerated electrolyte/electronic phase and gas phase. Suzuki et al. also assumed binary components of the catalyst layers and adopted the percolation theory to confirm the existence of an optimal ionomer composition [14]. However, substantial evidence from experimental studies indicates that ionomers are non-uniformly distributed on the carbon support and form inhomogeneous agglomerated catalyst and electrolyte structures in PEFCs [15,16], which can affect the transport phenomena, electrochemical surface area, and the corresponding reactions [17,18]. Malek et al. introduced a coarse-grained molecular dynamics (CGMD) modeling method to investigate the random inhomogeneous structural configurations of ionomers and porous morphology in a cathode catalyst layer [19,20]. Lee et al. also investigated the inhomogeneous ionomer distribution in an actual PEFC system and experimentally evaluated the catalyst effectiveness of platinum catalysts to improve the MEA performance [21,22].

However, in most common carbon black-based catalyst layers, agglomerated Pt/C structures may lead to low catalyst utilization because the catalysts exist on the surface of agglomerated carbon particles and inside the agglomerates; the reactants and ions cannot reach these areas for complete electrochemical reactions. In this regard, recently reported vertically aligned carbon nanotube (VACNT)-based catalyst layers are a promising approach. Extensive experimental studies have revealed that VACNTs have excellent electronic conductivity [23–25] and remarkable mass transport characteristics [26,27] because of well-organized Pt/Cs and pore structures in the catalyst layers, as shown in Fig. 1. Additionally, the VACNTs can provide a larger surface area for electrochemical reactions [24,28]. Indeed, several studies have reported that VACNT-based catalyst layers can enhance electron and mass transfer by using ordered porous CNTs as catalyst supports [29–32]. Tian et al. [31] presented a simple method to fabricate a membrane electrode assembly (MEA) for PEFC applications with VACNTs as catalyst supports. They confirmed that the catalyst loading can be significantly reduced by adopting VACNT catalyst layers, when compared to conventional carbon black-based catalyst layers. Murata et al. [32] also reported that VACNT catalyst layers can improve fuel cell performance. In their experimental study, VACNT catalyst layer structures increased the electron and mass transport paths by incorporating structurally controlled carbon nanotubes as catalyst supports.

Basically, the micro/nano-structures of catalyst layers are highly inhomogeneous and it is extremely difficult to repeatedly fabricate the catalyst layers with the same nano-morphology. However, most of previous studies relied on relatively few selected catalyst layers to estimate and compare the fuel cell performance.

In the present study, a three-dimensional quasi-random nanostructural modeling method is proposed to evaluate the potential capabilities of catalyst layers for electrochemical reactions in fuel cells. In addition, a catalyst utilization factor was defined to determine the relative amounts of catalysts participating in electrochemical reactions. Consequently, the catalyst utilization factor of VACNT electrodes was estimated by statistical three-dimensional morphology analysis in pursuance of the catalyst performance improvement. For the detailed morphological

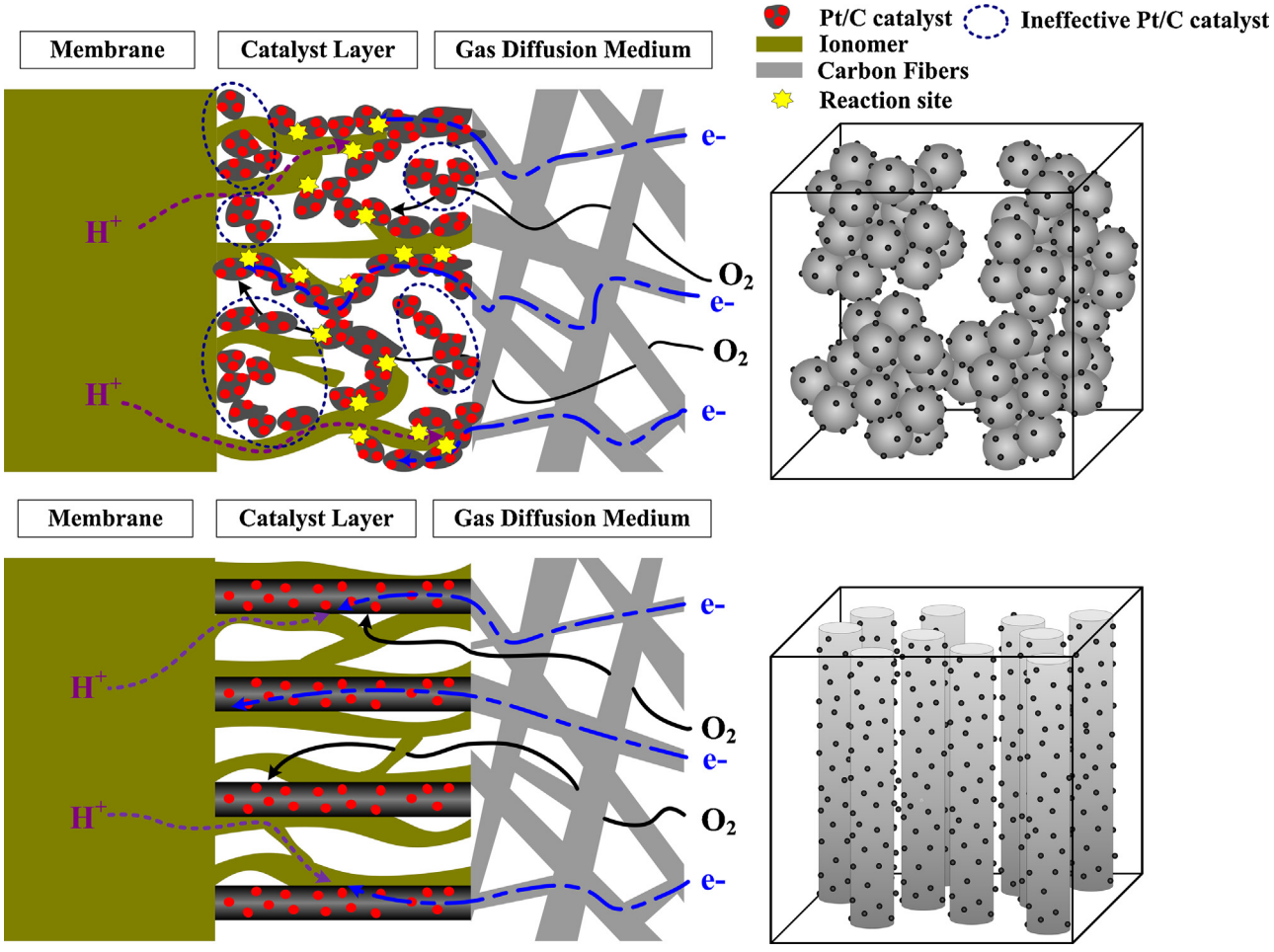

Fig. 1. A schematic diagram of the multi-phase random structure of conventional and VACNT catalyst layer structures for fuel cell applications.