



Nanoscale simulation of local gas transport in catalyst layers of proton exchange membrane fuel cells



Li Chen^{a,*}, Ruiyuan Zhang^a, Pu He^a, Qinjun Kang^b, Ya-Ling He^a, Wen-Quan Tao^a

^a Key Laboratory of Thermo-Fluid Science and Engineering of MOE, School of Energy and Power Engineering, Xi'an Jiaotong University, Xi'an, Shaanxi, 710049, China

^b Computational Earth Science, EES-16, Earth and Environmental Sciences Division, Los Alamos National Laboratory, Los Alamos, NM, 87544, USA

HIGHLIGHTS

- Nanoscale structures around a carbon particle are reconstructed.
- Pore-scale local transport around the carbon particle is simulated.
- Local transport resistance across the ionomer film is explored.
- Dissolution resistance increases the local transport resistance.
- Effects of microscopic structures on the local transport resistance are studied.

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ABSTRACT

Reducing Platinum amount in proton exchange membrane fuel cell (PEMFC) is one of the main tasks to achieve low cost PEMFC. Recently, significant performance loss has been found under low Pt loading due to local mass transport limitations. In this study, pore-scale simulations are conducted to study oxygen transport within four-constituent microscopic structures of catalyst layer including a carbon particle, ionomer, Pt particles, and primary pores inside the carbon particle. Multiphase physicochemical processes are considered, including oxygen dissolution at the pore/ionomer interface, oxygen diffusion within the ionomer film and inside the primary pores, and reactions at the Pt interface. Local transport resistance is calculated based on the pore-scale concentration field predicted. The simulation results are compared with existing experimental results and 1D models. Simulation results show that dissolution resistance at the secondary pore/ionomer interface is about 10–50 times higher than that inside the ionomer. Local transport resistance increases as Pt loading decreases, especially under Pt loading of 0.1 mg cm^{-2} . Besides, local transport resistance can be reduced by depositing more Pt outside the carbon particle, alleviating agglomeration and/or decreasing the ionomer thickness. The simulation results indicate that local transport characteristics should be considered when developing 1D agglomeration model of catalyst layer.

1. Introduction

Proton exchange membrane fuel cell (PEMFC) is a promising and attractive candidate for a wide variety of power applications such as fuel cell vehicles. Currently, there are several challenges remaining for commercialization of PEMFC including performance, durability and especially cost. Cost challenge of PEMFC mainly arises from the high cost platinum (Pt) catalyst. Currently, Pt is widely used in cell electrodes for accelerating the oxygen reduction reaction (ORR) and hydrogen oxidation reaction (HOR) in the cathode and anode catalyst layers (CL), respectively [1]. As Pt is expensive and the world supply of

Pt is limited, reducing Pt loading (Pt amount per unit surface area of catalyst layers, mg cm^{-2}) while maintaining the cell performance is one of the main tasks to achieve low cost PEMFC for commercial application. The US department of energy (DOE) sets a platinum-group-metal (PGM) target of 0.125 gPt kW by the year 2020, leading to Pt loading reduced to 0.1 mg cm^{-2} for the cathode.

Recently, Pt loading has been successfully reduced via development of highly active Pt alloy catalysts or core-shell catalysts [1]. Pt loading also can be reduced by enhancing transport inside the CL to increase the Pt utilization. CL is the most complex and critical, yet least understood, component in PEMFCs. It is porous for the purpose to increase reactive

* Corresponding author.

E-mail address: lichennht08@mail.xjtu.edu.cn (L. Chen).

Nomenclature

A	Total area of the reactive sites [m^2]
c	Lattice speed in LB model
C	Concentration [mol m^{-3}]
D	Diffusivity [$\text{m}^2 \text{s}^{-1}$]
F	Faraday's constant
g	Concentration distribution function in LB model
H	Henry constant
i_v	Volumetric current density [A m^{-3}]
J_{lim}	Current density [A m^{-2}]
k	Reaction rate constant [m s^{-1}]
L_{CL}	CL thickness [m]
m_{Pt}	Total weight of Pt in the computational domain [kg]
\hat{m}_{Pt}	Total weight of Pt per CL volume [kg m^{-3}]
n	number of electrons
N_{Pt}	Number of Pt particles
r	Radius of the carbon particle [m]
R_{other}	gas transport resistance [s m^{-1}]
t	Time [s]
\hat{v}_{Pt}	Total volume of Pt [m^3]
V	Volume [m^3]
x	coordinates

Greek symbols

β	Probability
ϵ_s	Porosity of secondary pores
γ_{Pt}	Pt loading [mg cm^{-2}]
ρ_{Pt}	Density of Pt [kg m^{-3}]
τ	Relaxation time in lattice Boltzmann model
ψ	Ratio of the number of Pt particles outside the carbon particle to the total number of Pt particles
Δx	Mesh size [m]

Subscripts

elec	Electrochemical reaction
dis	Dissolution reaction
g	Gas
N	Nafion
O_2	Oxygen
Pt	Platinum
s	Surface
W	Water

surface area and to provide pathways for the reactants, namely electrolyte for proton transport, carbon particles for electron conduction, and void space for gas and water transport. Electrochemical reaction takes place at the triple-phase boundary where the three reactants meet. Therefore, it is important to enhance transport processes in CL to improve cell performance and thus to reduce Pt loading.

Over the past years, extra voltage loss is found at low Pt loadings, which is hypothesized to be caused by Pt-oxide specific Tafel kinetics, or by additional oxygen transport resistance related to the thin ionomer film covering the carbon particles [2–12]. For the oxygen transport in the CL, transport resistance R_{total} consists of two parts [3], i.e., R_{se} the mass transport resistance in the secondary pores between carbon particles, and R_{other} the local transport resistance through the ionomer films to the Pt surface. The indirect method based on the limited current density has been widely adopted to determine the transport resistance, in which R_{total} is calculated by $C/(i_{\text{lim}}/nF)$ with C the oxygen concentration supplied and i_{lim} the limiting current density generated. Greszler et al. [5] found that the mass transport resistance R_{other} is about 5 s m^{-1} at 0.4 mg cm^{-2} Pt loading, which greatly increases to 20 s m^{-1} at 0.1 mg cm^{-2} Pt loading [5]. If one calculates such O_2 transport resistance using known O_2 permeability of a thick ionomer membrane, an ionomer film with thickness of 35 nm is predicted to cover the Pt/C. However, according to common experimental observation, the typical thickness of ionomer film is much thinner (only about 3 nm in CL [5]). The origin of such high oxygen transport resistance has been widely studied in the literature. Yoon and Weber pointed out that as Pt loading decreases, oxygen has to transport a longer length to reach the Pt surface, partially accounting for the higher mass transport resistance [13]. Ex-situ measurements found that thin-film ionomer show different nanostructures and physicochemical properties (water uptake, proton conduction, O_2 permeability) [14–18]. Sulfonate ion absorption near the Pt/ionomer interface also modifies the ionomer structures, causing additional mass transport resistance at the Pt surface [12]. Kudo et al. [10,11] adopted a microelectrode technique for casting thin nafion film and found that there is interfacial resistance at the pore/ionomer and ionomer/Pt interface. Using molecular dynamic (MD) simulations, Jinnouchi et al. [19] found that there exist free energy barriers both at the pore/ionomer and ionomer/Pt interfaces, leading to reduced O_2 solubility and permeability. Very recently, by using MD simulations based on more accurate force fields obtained from density functional

theory (DFT) calculations, Kurihara [20] investigated effects of water content on oxygen diffusivity, solubility and permeability in the thin ionomer, and identified the highest mass transport resistance at the ionomer/Pt interface. From above studies, it can be concluded that quantification of each resistance across the thin ionomer, namely that at the pore/ionomer interface, that inside the ionomer, and that at the ionomer/Pt interface, is of great importance. However, in practice all these resistances are closely coupled and interact with each other, and hence may not be readily separated [18].

Due to the nanoscale and complex structures of the CL, direct measurement and observation of transport processes within the CL has remained an impossible task. As a complementary method to experiments, numerical simulations help to gain deep understanding of reactive transport inside the CL. Continuum-scale models of CL with varying degrees of resolution can be categorized into thin-layer model [21], homogeneous model [22] and agglomerate model [23]. Recently, pore-scale simulations, which are based on the microscopic structures of CL, have become the most recent trend in CL modeling. Wang et al. [24] reconstructed a two-constituent micro-structure of CL with the pore constituent and the solid constituent which is a mixture of carbon and ionomer. Finite element method was adopted to solve oxygen and proton transport processes. Lange et al. [25] reconstructed three-constituent CL structures with pore, ionomer and the solid which is a mixture of carbon and Pt. Effects of Knudsen diffusion on effective diffusivity were taken into account. Four-constituent CL microscopic structures taking into account all the CL constituents (pore, carbon, ionomer and Pt) also have been reconstructed by mimicking the fabricating processes [26], and effects of volume fraction of different constituents on the Pt utilization were explored in detail. Chen et al. [27] also reconstructed four-constituent CL structures, and compared the characteristics of the reconstructed structures (pore size distribution, specific surface area, connectivity, and tortuosity) with existing experimental results. Effective diffusivity under different porosity was predicted and it was found that Bruggeman equation overestimates the effective diffusivity. Multiphase flow in CL was also investigated at the pore-scale [28]. Very recently, Fathi et al. [29] simulated pore-scale immiscible two-phase flow in CL and predicted the effective diffusivity under different water saturation. The above pore-scale studies provide deep understanding of effects of microscopic structures on transport phenomena in and macroscopic transport properties of CL.

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