The Impact of Platinum Reduction on Oxygen Transport in Proton Exchange Membrane Fuel Cells

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ABSTRACT

Key challenges to the acceptance of Proton Exchange Membrane Fuel Cells (PEMFCs) for Fuel Cell Electric Vehicles (FCEVs) are the cost reduction and improvements in power density for compactness.

High current density operation is one of the most effective solutions for cost reduction and power density improvements. It contributes to size reduction of PEMFCs as well as lower amounts of Platinum (Pt). However, high current density operation causes an increase in concentration overpotential, resulting in lower cell performance. In addition, the oxygen transport resistance typically increases under lower Pt loadings.

The effect of rib/channel widths and Pt loading on oxygen transport resistance and cell performance were investigated by coupled experimental and numerical analyses in this study. Oxygen transport resistance was obtained by measuring limiting current with various rib/channel widths and platinum loadings, and it significantly increased depending on the rib/channel widths as well as platinum loadings. A three-dimensional numerical model was developed by implementing the oxygen transport resistance from the pores in catalyst layer to the platinum surface. Numerical validations showed that the rib/channel widths caused inhomogeneous reaction distributions in both in-plane and through-plane directions. This resulted in an increase in the oxygen transport resistance. Also, the numerical model revealed that the oxygen flux per platinum surface area significantly increased when platinum loading is decreased, causing an increase in the oxygen transport resistance. Moreover, the model could reproduce the cell performances under high current density with different rib/channel widths and platinum loadings. These results suggested that a reduction of oxygen flux per platinum surface area was essential to achieve high current density operation with lower platinum loadings.

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1. Introduction

Proton Exchange Membrane Fuel Cells (PEMFCs) are a promising power source of clean energy for automotive use. In PEMFCs, the chemical energy of a fuel is directly converted into electricity by electrochemical reactions that are catalyzed by platinum (Pt). Since Pt is a precious metal, a reduction of total Pt required is essential to achieve commercialization of Fuel Cell Electric Vehicles (FCEVs)[1,2].

High current density operation is one of the most effective solutions since it contributes to a reduction in PEMFCs size as well as a reduction in the amount of Pt required[3]. However, under high current density operation, concentration overpotential due to oxygen transport shows a significant impact on stack performance. Moreover excessive water is generated that can accumulate inside the PEMFC, which hinders oxygen transport. In addition, high current density operation also results in high heat generation. Excessive heat generation affects not only performance loss due to dry-out but also degradation. From this background, proper management of mass transport phenomena inside a PEMFC is extremely important. Deeper understanding of oxygen transport is necessary to achieve the high current density operation in a PEMFC stack.

So far, various studies have been attempted to characterize the oxygen transport resistances. Baker *et al.* measured the effective oxygen diffusivities in GDLs and MPLs, and elucidated that approximately half of the total oxygen transport resistance was attributed to the GDL. They also estimated the magnitude of the oxygen transport resistance inside the gas channel [4]. Sakai *et al.* extracted the effect of Pt loadings on oxygen transport resistances by using a one-dimensional (1-D) reactant gas transport model. They showed that the pressure-independent oxygen transport resistance increased when Pt loadings was lower [5]. Nonoyama *et al.* utilized a porous metal plate to avoid in-plane gas distribution induced by rib/channel widths and analyzed the contribution of the catalyst layer to total oxygen transport resistance [6]. They concluded that permeation through the ionomer film surrounding

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Nomenclature

A	defined in Equation(21)
C_{sat}	concentration of the saturated water vapor mol m^{-3}
C_p	specific heat J kg^{-1} K^{-1}
C	concentration mol m^{-3}
D	diffusion coefficient m^2 s^{-1}
F	Faraday constant =96485 C mol^{-1}
i	transfer current density (Pt area based) A m^{-2}
i_e	protonic (electrolyte phase) transfer current density A m^{-3}
i_{lim}	limiting current density A m^{-2}
i_s	electron(solid-phase) transfer current density A m^{-3}
J	Leverett function
j	volumetric transfer current density A m^{-3}
j_0	exchange current density A m^{-3}
j_l	capillary diffusion mass flux kg s^{-1}
K	absolute permeability m^2
k_{rg}	relative permeability of gas phase
k_{rl}	relative permeability of liquid phase
M	molecular weight of gas kg mol^{-1}
m	molecular weight of liquid kg mol^{-1}
mf_l	mass fraction of liquid
n	direction normal to the surface
n_d	electro-osmotic drag coefficient
n_k	number of electrons transferred (for species k)
p	pressure Pa
R	universal gas constant =8.314 J mol^{-1} K^{-1}
$R_{O2,total}$	total oxygen transport resistance s m^{-1}
$R_{O2,CCL-micro}$	micro transport resistance near Pt surface s m^{-1}
S	source term
s	liquid saturation
T	temperature K
$\bar{u}$	velocity m s^{-1}
V	potential V
vrf	volumetric roughness factor m^2 m^{-3}

Greek letters

α	transfer coefficient in Butler-Volmer equation
γ_c	advective correction factor
ε	porosity
η	overpotential V
θ_c	contact angle
κ	proton conductivity S m^{-1} or thermal conductivity W m^{-1} K^{-1}
λ	relative mobility
ν	kinematic viscosity m^2 s^{-1}
ρ	mass density kg m^{-3}
σ	electrical conductivity S m^{-1} or surface tension N m^{-1}
τ	shear stress N m^{-2}
φ_s	potential of solid phase (electrical potential) V

Superscripts

eff	effective
k	species k

Subscripts

c	cathodic
cell	cell voltage
channel	gas flow channel
g	gas phase
k	species k
l	liquid phase
lim	limiting current
O2	oxygen
proton	proton
Pt	Pt surface
ref	reference
u	momentum conservation
w	water
φ_e	electrolyte potential
φ_s	electrical potential
0	wall properties

the catalyst layer was a major portion of total oxygen transport resistance. On the other hand, the oxygen transport resistance in the secondary pores of the catalyst layer was much smaller. Limiting current measurement has often been adopted to quantify the oxygen transport resistances in PEMFCs [4–6]. In this technique, oxygen transport resistances are quantified based on a one-dimensional gas transport assumption in most cases. The separator usually consists of a rib and a channel, and every fuel cell component (gas diffusion media, catalyst layer, and membrane) also has thickness. Additionally, gas concentration has a distribution along the flow direction due to gas consumption and water generation. In other words, transport phenomena in PEMFC are genuinely multi-dimensional. Due to its complex nature, the quantitative analysis of transport phenomena, including geometric factors of PEMFCs and Pt loadings, is poorly understood, regardless of its importance. Therefore, it is necessary to analyze these phenomena by specifically considering geometric effects.

Numerical models have been employed in combination with experimental results to complement the theory. Weber *et al.* reported the effect of liquid water on cell performance [7,8]. Their numerical model considered liquid water transport by capillary pressure inside porous media, such as catalyst layers, MPLs and GDLs. The model predicted a different liquid water saturation ratio (liquid water volume/pore volume) under channels than under ribs. The distribution of liquid water saturation ratio in porous media was helpful in understanding water transport in operating PEMFCs. However it was considered through-plane direction only. Eikerling *et al.* introduced a structure-based model for the cathode catalyst layer [9,10]. Their model took into account pore size distribution and wetting properties of catalyst layer and revealed their fundamental roles on cell performance. Their model also considered through-plane direction only, in other words, it was one-dimensional model. Ono *et al.* modified the 1-D model by implementing the effect of both platinum oxide and oxygen transport resistance near Pt surface. Their model was helpful with understanding the transport phenomena in catalyst layer. The model from Ono *et al.* didn't take into account rib/channel widths because the model was a 1-D model [11]. In practical PEMFCs for automobile applications, the separators generally have rib/channel geometry. Electrons are mainly transferred through the rib region. Fuel and oxidant gases are supplied from the channels to the reaction sites. Temperature and water distributions in the MEA between ribs and channels are not negligible. From these aspects, a one-dimensional model cannot address the rib/channel effects on cell performance.

Among numerical models, multi-dimensional, multi-phase, and non-isothermal macro homogeneous cell models are the most powerful. This is because conservation equations (mass, momentum, species, charge, and energy) are fully coupled in multi-dimensional, multi-phase, non-isolthermal, macro homogeneous models. Multiphase Mixture (M2) model is an example of such a model [12–17]. This set of these equations was solved in