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Multivariable optimization studies of cathode catalyst layer of a polymer electrolyte membrane fuel cell

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ABSTRACT

The amount of current generated in a polymer electrolyte membrane fuel cell (PEMFC) depends strongly on the local conditions in a cathode such as available oxygen, surface area available for the reactions, amount of ionomer, and amount of electro-catalyst. In the present work, design parameters of a cathode catalyst layer are optimized to achieve the maximum current density at a given operating voltage. The decision variables are chosen such that they can be realized experimentally. To understand the effect of the model fidelity on the decision variables, optimization is performed with a single phase model and a two-phase model with and without membrane. Other objective functions such as maximization of current generation per catalyst loading, minimization of catalyst layer cost per power and minimization of cell cost per power are also considered to study the effects of the objective functions on the decision variables.

Keywords: PEMFC; Two-phase modeling; Multivariable optimization; Platinum utilization

1. Introduction

Extensive research and development efforts are being undertaken in recent years in the field of PEM fuel cell (PEMFC) systems to make them commercially viable. However, further cost reduction and performance improvement are required to make PEMFCs a commercial success. The major cost component of a PEMFC is the platinum catalyst. The platinum loading is typically about 0.05–0.2 mg cm^{-2} on the anode side and 0.2–0.6 mg cm^{-2} on the cathode side (Gasteiger et al., 2004, 2005). More platinum is used on the cathode side because of the sluggish oxygen reduction reaction. As many limiting processes take place in the reaction layer, it is important to model this layer. Most of the models developed earlier (Springer et al., 1991; Bernardi and Verbrugee, 1991; Bernardi and Verbrugge, 1992; Berning et al., 2002; Pasaogullari and Wang, 2004) have considered the catalyst layer (CL) as very thin and ignored its effect on the performance of the cell. Even though these layers are 5–20 μm thick, neglecting the effect of this finite thickness can lead to errors in predicting the performance of the fuel cell. The catalyst layer can be modeled using a macro-homogenous approach or agglomerate characterization (Rao et al., 2007). By using advanced microscopy instruments like scanning electron microscope (SEM) and transmission electron microscope (TEM), various researchers have studied the morphology of the catalyst layer. Middleman (2002) has reported that the catalyst layer consists of random distribution of particles and pores. The tiny particles form agglomerates with a thin film of ionomer. These agglomerates are either spherical or cylindrical in shape. Lin et al. (2004, 2006) have used cylindrical agglomerate characterization, whereas Sun et al. (2005) and Rao et al. (2007) have used spherical agglomerate characterization for modeling the catalyst layer. Another major cost component of a PEMFC is the polymer membrane. Nafion is the commonly used membrane in a PEMFC. These membranes are expensive and can give poor performance under low humidity and high temperature conditions (Viswanathan and Helen, 2007).

The performance of the cell depends mainly on the operating conditions, design of the flow field, composition and

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Nomenclature

c_f	fixed charge site concentration ($mol\,m^{-3}$)
C_i^k	concentration of species i in region k ($mol\,m^{-3}$)
C_W^{mem}	concentration of liquid water in the membrane ($mol\,m^{-3}$)
$D_i^{eff,k}$	effective diffusivity of the species i in region k ($m^2\,s^{-1}$)
D_W^{mem}	diffusivity of liquid water in the membrane ($m^2\,s^{-1}$)
E	activation energy ($J\,mol^{-1}$)
$f_{ionomer}$	weight fraction of ionomer in the catalyst layer
f_{Pt}	weight fraction of platinum on carbon
F	Faraday's constant ($C\,mol^{-1}$)
i_a	local current density ($A\,(m^2\,Pt)^{-1}$)
i_{cell}	cell current density ($A\,(m^2\,Pt)^{-1}$)
i_o	exchange current density for oxygen reduction on platinum ($A\,m^{-2}$)
i_o^{ref}	reference exchange current density for oxygen reduction on platinum ($A\,m^{-2}$)
I_w	interfacial transfer of water between liquid and vapor ($mol\,m^{-3}\,s^{-1}$)
J_i^k	local flux due to diffusion of species i in region k ($mol\,m^{-2}\,s^{-1}$)
k_c	condensation constant (s^{-1})
k_v	evaporation constant ($atm^{-1}\,s^{-1}$)
$K_{wo,k}$	permeability of liquid water inside porous region k at 100% saturation (m^2)
m_{Pt}	platinum loading inside the catalyst layer ($kg\,Pt\,(m^2\,CL)^{-1}$)
n	number of electrons taking part in the oxygen reduction reaction
n_d	net electro-osmotic drag coefficient
$N_{W,k}$	flux of liquid water in region k ($mol\,m^{-2}\,s^{-1}$)
r_{agg}	agglomerate radius (m)
R	universal gas constant ($J\,mol^{-1}\,K^{-1}$)
R_{O_2}	rate of oxygen reduction reaction per unit volume of the catalyst layer ($mol\,m^{-3}\,s^{-1}$)
S_ϕ	source term
t_{CL}	thickness of the catalyst layer (m)
T_{cell}	cell temperature (K)
V_{cell}	cell voltage (V)
w_c	mass of carbon inside the agglomerate (kg)
$w_{ionomer}$	mass of ionomer inside the agglomerate (kg)
w_{Pt}	mass of platinum inside the catalyst layer (kg)

Greek letters

β	cathode transfer coefficient
ε_k	void fraction inside region k
$\varepsilon_{ionomer}$	fraction of volume occupied by the ionomer inside the catalyst layer
$\kappa^{eff,c}$	effective proton conductivity in the catalyst layer ($mho\,m^{-1}$)
$\kappa^{eff,mem}$	effective proton conductivity in the membrane ($mho\,m^{-1}$)
κ_{ele}^k	electric conductivity in region k ($S\,m^{-1}$)
$\kappa_{ele}^{eff,k}$	effective electric conductivity in region k ($S\,m^{-1}$)
λ_w	water content in the membrane ($mol\,H_2O\,(mol\,SO_3)^{-1}$)
ρ_c	density of carbon ($kg\,m^{-3}$)
$\rho_{ionomer}$	density of ionomer ($kg\,m^{-3}$)
ρ_{Pt}	density of platinum ($kg\,m^{-3}$)
ρ_w	density of water ($kg\,m^{-3}$)

design parameters of the membrane electrode assembly (MEA), and MEA preparation techniques. Optimization of cell performance will require a fundamental understanding of the various processes taking place inside the cell and their influence on the cell performance. However, it is difficult to study all these processes through experiments. Hence, a detailed mathematical model is useful in simulating the effect of various model parameters on the performance of the cell. For this purpose, a two-dimensional, two-phase model has been developed. The developed model is useful for studying the effects of various operating, design, and model parameters on the cell performance. In a typical fuel cell, the concentration of the reactants decreases from inlet of the gas flow channel to the outlet. Spatial variations exist within the catalyst layer as well. The amount of current generated in the catalyst layer depends on the local conditions such as available oxygen, surface area available for reaction, the amount of ionomer, and the amount of catalyst. These local conditions in turn depend on the volume fractions of voids, ionomer, and the solids. For a given thickness of the catalyst layer, the void fraction (ε_r) in the catalyst layer depends on design parameters such as, catalyst loading (m_{Pt}), weight fraction of Platinum on Carbon (f_{Pt}), weight fraction of ionomer inside the catalyst layer ($f_{ionomer}$) and density of ionomer ($\rho_{ionomer}$). In the optimization studies presented in this work, all the above parameters are incorporated in the steady state model so that the interactions between them are captured in the predictions. Gasteiger et al. (2003) have experimentally shown the importance of catalyst layer design parameters in reducing the MEA losses. Catalyst layers are usually prepared using a mixture of carbon supported platinum particles, ionomer solution and solvent. After evaporation of the solvent, the final CL contains solids (carbon and platinum), ionomer and voids. Hence, the decision variables used in this optimization study are platinum loading, ionomer loading, weight fraction of platinum on carbon and CL thickness. Optimization is performed throughout the polarization range using a single phase and a two phase model to show the importance of liquid water modeling on the optimization results. Dependence of the optimization results on the initial guess is also studied. A number of different objective functions are considered. It is observed that the values of the decision variables strongly depend on the objective function considered and the constraints imposed.

2. Background

A typical objective of a cell level optimization study is to maximize the current density at a given operating voltage. A number of publications can be found in this area. Secanell et al. (2007a,b) have optimized the PEMFC cathode by numerical optimization techniques. In their earlier work (Secanell et al., 2007a), the authors have optimized the composition of the catalyst layer and showed that current density can be increased by more than 50%. This increase is due to substantial reduction in the porosity and an increase in platinum loading and volume fraction of the ionomer. In their recent work, Secanell et al. (2007b) have performed multivariable optimization studies of the PEMFC cathode. The optimization variables are