Multi-variable optimisation of PEMFC cathodes based on surrogate modelling

CrossMark

Lei Xing [a,b], Xueguan Song [c,], Keith Scott [a], Volker Pickert [c], Wenping Cao [c]*

[a] *School of Chemical Engineering and Advanced Materials, Merz Court, Newcastle University, Newcastle upon Tyne NE1 7RU, UK*
[b] *School of Chemical Engineering, Inner Mongolia University of Technology, Hohhot 010051, China*
[c] *School of Electrical and Electronic Engineering, Merz Court, Newcastle University, Newcastle upon Tyne NE1 7RU, UK*

ARTICLE INFO

ABSTRACT

A two-dimensional, steady state, isothermal agglomerate model for cathode catalyst layer design is presented. The design parameters, platinum loading, platinum mass ratio, electrolyte volume fraction, thickness of catalyst layer and agglomerate radius, are optimised by a multiple surrogate model and their sensitivities are analysed by a Monte Carlo method based approach. Two optimisation strategies, maximising the current density at a fix cell voltage and during a specific range, are implemented for the optima prediction. The results show that the optimal catalyst composition depends on operating cell voltages. At high current densities, the performance is improved by reducing electrolyte volume fraction to 7.0% and increasing catalyst layer porosity to 52.9%. At low current densities, performance is improved by increasing electrolyte volume fraction to 50.0% and decreasing catalyst layer porosity to 12.0%. High platinum loading and small agglomerate radius improve current density at all cell voltages. The improvement in fuel cell performance is analysed in terms of the electrolyte coating thickness, agglomerate specific area, conductivity, overpotential, volumetric current density and oxygen mole fraction within the cathode catalyst layer. The optimisation results are also validated by the agglomerate model at different cell voltages to confirm the effectiveness of the proposed methodologies.

1. Introduction

A proton exchange membrane fuel cell (PEMFC) converts the chemical energy from a fuel into electricity through a chemical reaction with oxygen or another oxidizing agent. It is widely known as an environmentally friendly energy resource because the only by-products are water and heat [1]. Although significant improvements on PEMFC performance have been achieved over the last ten years, the high cost associated with platinum catalyst is one of the major barriers hampering the commercial use of PEMFCs. Since platinum is dispersed within carbon black and combines with electrolyte to construct the catalyst layer, the performance depends on how effectively the platinum is dispersed, i.e. the effectiveness of the catalyst layer [2]. Accordingly, the function of different component within the catalyst layer requires the existence of triple phase boundaries (TPB) [3], where the content of electrolyte (for proton transfer), void

Nomenclature

A	cross-sectional area, m^2
A_s	reaction surface area per unit platinum mass, $m^2\,kg^{-1}$
a	specific area, m^{-1}
c	concentration, $mol\,m^{-3}$
c_f	fixed charge concentration in membrane, $mol\,m^{-3}$
D	diffusivity, $m^2\,s^{-1}$
D_{ij}	Maxwell—Stefan diffusion coefficient matrix, $m^2\,s^{-1}$
$\tilde{D}_i$	partial variance
d	pore diameter, m
E	effectiveness factor
E^0	open circle potential, V
E_{cell}	cell voltage, V
F	Farady's constant, $96485\,C\,mol^{-1}$
$\mathbf{f}$	column vector of length n_s
f	platinum mass ratio to Pt/C
H	Henry's constant, $Pa\,m^3\,mol^{-1}$
i	current density, $A\,m^{-2}$
i_0	exchange current density, $A\,m^{-2}$
k	reaction rate coefficient, s^{-1}
l	thickness, m
L	volume fraction
M_j	molecular weight for specie j, $kg\,mol^{-1}$
M_n	mean molecular weight, $kg\,mol^{-1}$
m_{Pt}	platinum loading, $mg\,cm^{-2}$
m_C	carbon loading, $mg\,cm^{-2}$
N	number per volume
N_j	molar flux of specie j, $mol\,m^{-2}\,s^{-1}$
n	number
p	pressure, Pa
Q	reactant gas flow rates, $m^3\,s^{-1}$
$\mathbf{R}$	symmetric correlation matrix
R	reaction rate, $mol\,m^3\,s^{-1}$
R_g	ideal gas constant, $8.314\,J\,mol^{-1}\,K^{-1}$
R_M	membrane resistance, $\Omega\,m^{-2}$
RH	relative humidity
r	radius, m
S	global sensitivity
T	temperature, K
u	flow velocity, $m\,s^{-1}$
V	mole volume, m^3
w	mass fraction
$\mathbf{x}$	design matrix of sample
X	normalised distance (x/δ_{CL})
x	mole fraction
$\tilde{x}_i$	design variable i
Y	normalised distance (y/l)
$\mathbf{y}$	column vector
$\%M$	volume fraction of primary pores occupied by electrolyte

Greek

α	charge transfer coefficient
α_{H_2O}	water activity
β	unknown coefficient
κ_p	hydraulic permeability, m^2
λ	water content
μ	viscosity, Pa s
ρ	density, $kg\,m^{-3}$
τ	shear stress tensor
ε	porosity
$\tilde{\varepsilon}_i$	individual error
γ	oxygen diffusion rate through the electrolyte film, s^{-1}
θ_k	unknown correlation parameters
δ	film thickness, m
η	overpotential, V
σ_M	proton conductivity of electrolyte, $\Omega^{-1}\,m^{-1}$
σ^2	variance
ξ	stoichiometric flow ratio
ζ	random point
M_T	Thiele's modulus
ϕ	potential, V
ψ_{H_2O}	association parameter for water (the value is 2.6)

Superscripts

0	intrinsic
agg	agglomerate
eff	effective
ref	reference
eq	equilibrium

Subscripts

a	anode
agg	agglomerate
avg	average
C	carbon
c	cathode
CL	catalyst layer
dv	design variable
GDL	gas diffusion layer
g	gas mixture
i	species i
j	species j
Kn	Knudsen diffusion
M	electrolyte
P	void space
Pt	platinum
Pt/C	platinum dispersed carbon
p	primary pores
pc	percolation critical value
S	GDL penetration
s	secondary pores
W	liquid water
sat	saturation
tot	total

space (for gas transport) and platinum dispersed carbon (for catalysis and electron transfer) interacted [4—8]. As a result, optimisation of the composition and structure of the electrode is important.

Traditionally, the optimum composition and structure of the catalyst layer is conducted through experiments [5—8], which are expensive and time-consuming. Computer simulations facilitate the exploration of alternative designs and