Performance Modeling and Current Mapping of Proton Exchange Membrane Electrolyzer Cells with Novel Thin/Tunable Liquid/Gas Diffusion Layers

Zhenye Kang, Jingke Mo, Gaoqiang Yang, Yifan Li, Derrick A. Talley, Bo Han, Feng-Yuan Zhang*

Nanodynamics and High-Efficiency Lab for Propulsion and Power (NanoHELP), Department of Mechanical, Aerospace & Biomedical Engineering, UT Space Institute, University of Tennessee, Knoxville (UTK), Tullahoma, TN 37388, USA

ABSTRACT

The novel titanium thin/tunable liquid/gas diffusion layers (TT-LGDLs) with precisely controllable pore morphologies have achieved superior multifunctional performance in proton exchange membrane electrolyzer cells (PEMECs) with its advantages of ultra-thin thickness (25 μm), planar surface, and straight-through pores. By taking advantage of the precise pore morphology of TT-LGDLs, a comprehensive computational model is developed in MATLAB/Simulink platform to simulate the CL current distribution, and PEMEC electrochemical performance. The interfacial contact resistances between the TT-LGDLs and catalyst layers (CLs), and PEMEC overpotentials are closely correlated to the TT-LGDL pore diameter and porosity. In addition, the roughness factor, which is a critical coefficient in simulating the activation overpotential in Butler-Volmer equation, is also modeled as a function of TT-LGDL morphologies. More importantly, a novel two-dimensional (2D) CL resistance model that consists of both in-plane and through-plane resistances is also developed to predict the current distribution on the CLs. The present model can precisely match the experimental results and effectively calculate the PEMEC performance with different TT-LGDL morphologies and operating temperatures. Results obtained from the present model will provide a deep understanding of the functions of TT-LGDL morphology, and also help to optimize the design and fabrication of both the TT-LGDLs and CLs.

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1. Introduction

Proton exchange membrane electrolyzer cells (PEMECs), which work as the reverse PEM fuel cells (PEMFCs), have been considered as one of the most attractive and popular methods for hydrogen and oxygen generation from water splitting, especially when coupled with the renewable energy sources such as wind, solar, hydro, tide, etc. [1–7]. PEMECs can produce very pure hydrogen/oxygen with few contaminants and have many advantages, including high energy efficiency, fast charging/discharging, and compact design [8–11]. In addition, PEMECs provide a completely environmentally friendly approach to produce hydrogen compared with the conventional methods, such as alkaline water electrolysis and fossil fuel reforming, and it can be operated effectively under low temperatures [12–16].

Fig. 1 shows the main components in a typical PEMEC, which is similar to the structure of PEMFCs [17]. It consists of two electrodes, including anode and cathode, which are separated by a proton exchange membrane (PEM). At each electrode, there are a bipolar plate (BP) with flow channels (FCs) on it, a liquid/gas diffusion layer (LGDL), and a catalyst layer (CL). Liquid water at the anode is continuously supplied and it flows from the BP/FCs through the LGDLs to the surface of the CLs, where water is electrochemically split into oxygen molecules, protons, and electrons after the electricity is applied to the PEMECs. Protons, generated at anode, transport from the electrochemical reaction sites through the PEM to the cathode to form hydrogen gas. The electrochemical performance of the PEMECs is influenced by many factors, including operating conditions, PEM physical parameters, CL properties, LGDL pore morphologies and so on [18]. Modeling is one of the promising methods to optimize PEMEC designs and operations due to its precisely predicting results, time saving, and low cost.

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* Corresponding author.
  E-mail address: fzhang@utk.edu (F.-Y. Zhang).

Nomenclature

List of symbols

A	Reaction area, cm^2
a_0	Empirical coefficient to estimate the interfacial saturation
$a_{r,an}$	Roughness factor of anode in Bulter-Volmer equation
$a_{r,cat}$	Roughness factor of cathode in Bulter-Volmer equation
$C_{O_2,m}$	Oxygen concentration at the interface of electrode and membrane, mol/cm^3
$C_{H_2,m}$	Hydrogen concentration at the interface of electrode and membrane, mol/cm^3
D	The pore diameter of the TT-LGDLs, μm
d_0	Dimensionless relative pore diameter
i	Current density, A/cm^2
i_0	Exchange current density, A/cm^2
k	Permeability, m^2
N	The total number of pores in the TT-LGDLs
p	Pressure, atm
R_{in}	Interfacial contact resistance, Ω
R_{ip_m}	In-plane resistance of the CLs at the m torus, Ω
R_{tp_m}	Through-plane resistance of the CLs at the m torus, Ω
R_{LGDL}	LGDL resistance, Ω
R_{PEM}	PEM resistance, Ω
R_{BP}	Bipolar plate resistance, Ω
S	The number of total reaction sites
s	Liquid saturation
t	Time, s
T	Temperature, K
V	Voltage or overpotential, V
V_0	Reversible voltage, V
z	Mole number of electrons

Greek

α_a	Anode charge transfer coefficient
α_c	Cathode charge transfer coefficient
ε	Porosity
ε_0	Dimensionless relative porosity
θ	Contact angle of TT-LGDLs, degree (^{o})
μ	Fluid dynamic viscosity, $N\ s/cm^2$
ρ	Resistivity, $\Omega\ cm$ or Fluid density, kg/cm^3
σ	Surface tension, N/cm
σ_m	PEM conductivity, S/cm
δ_m	PEM thickness, micron (μm)
λ	PEM humidification degree

Constants

ρ_{H_2O}	Water density, $1.0\ g/cm^3$
μ_{H_2O}	Water dynamic viscosity, $3.5 \times 10^{-7} N\ S/cm^2$
F	Faraday constant, 96485.0 C/mol
K	K coefficient, $1.4 \times 10^{-2} \Omega$
M_{H_2}	Hydrogen molar mass, 2.0 g/mol
M_{H_2O}	Water molar mass, 18.0 g/mol
M_{O_2}	Oxygen molar mass, 32.0 g/mol
R	Gas constant, 8.314 J/mol K

water transport phenomenon through the membrane in PEMECs with Simulink[20]. Z. Abdin et al. also used Simulink to model and simulate the PEMEC performance, which is a powerful tool for exploring the effects of each component [21]. Grigoriev et al. introduced a model to evaluate PEMEC performance under atmosphere and high pressure. The effects of different operating pressure, temperature, and current density were also discussed comprehensively [22,23]. Marangio et al. also developed a theoretical model especially for high pressure PEMECs, which used Gibbs free energy to calculate the open circuit voltage. The water transport in PEMECs were also comprehensively investigated by considering the concentration difference, electroosmotic drag, pressure difference, and so on. The interfacial contact resistances was also considered in the model which had a great influence on PEMEC performance [24]. David et al. established a three-dimensional (3D) model of CLs in PEMFCs by taking into account the detailed composition and structure of the CLs using a multiple thin-film agglomerate model [25]. Our group also established a electrochemical performance model of a PEMEC which fully considered the effects of various operating conditions and design parameters on the cell performance based on the porous conventional LGDLs [26,27]. The two-phase transport model was developed to investigate the transport properties in the anode porous LGDL and to analyze their effects on the PEMEC performance and efficiency [28–31].

By taking advantage of advanced micro/nano manufacturing [32], a novel thin planar titanium LGDL with tunable pore morphologies has achieved superior performance with a large porosity and small circular pore diameter, as shown in Fig. 2, and this kind of thin/tunable LGDLs (TT-LGDLs) can significantly reduce the ohmic and activation losses [33–35]. Although a lot of models have been established for PEMECs and PEMFCs, they all use conventional porous media as their LGDLs, such as Ti felts as shown in Fig. 2 [19,36–38]. It has been found that the structures of the TT-LGDLs are significantly different from conventional porous Ti felt LGDLs, and the thickness of the novel TT-LGDLs is only 25 μm, which is much thinner than conventional Ti felt (350 μm). The planar surface of the TT-LGDLs can greatly enhance the interfacial contact characteristics, while the Ti felt is made of fibers and the interface is impacted by compression conditions. An impressive phenomenon has shown that the oxygen bubbles only generate at the rim of the pores along the CL surface, which has been captured by a high-speed and micro-scale visualization system [34,39]. The conventional models cannot successfully simulate the PEMECs with TT-LGDLs by simply changing some parameters in the codes because they are developed for the thick conventional LGDLs without precise pore morphologies, such as Ti felts, sintered Ti powders, carbon papers, carbon clothes, etc. In addition, these conventional LGDLs are usually simplified or combined with CL as a single component in the conventional PEMEC models [21,24,27]. With the novel TT-LGDL development, a comprehensive model for precisely assessing the impacts of TT-LGDL morphologies on the PEMEC performance and better optimizing the design parameters and operating conditions is strongly desired.

In this study, a comprehensive computational model for the PEMECs with TT-LGDLs at anode side is established based on the previous model for conventional PEMECs [30]. MATLAB/Simulink is adopted to develop this novel model due to its user-friendliness, modular programming, very good interactivity and portability [40]. A new ohmic loss submodel for PEMECs, including the interfacial contact resistances between the CLs and TT-LGDLs, has been proposed. Furthermore, the roughness factor in the Butler-Volmer equation, which is used to calculate the activation overpotential, can greatly influence the PEMEC performance by pore morphology of the TT-LGDLs, and its relation has been embedded in the comprehensive computational model. The

Choi et al. developed a simple mathematical model that calculated the cell voltage of solid polymer electrolyte water electrolysis, including interfacial contact ohmic overpotential. They also used simplified Butler-Volmer equation to calculate the activation overpotential [19]. Gorgun's model focused on studying