Journal of Power Sources 402 (2018) 468–482

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Hydrophilic microporous layer coatings for polymer electrolyte membrane fuel cells operating without anode humidification

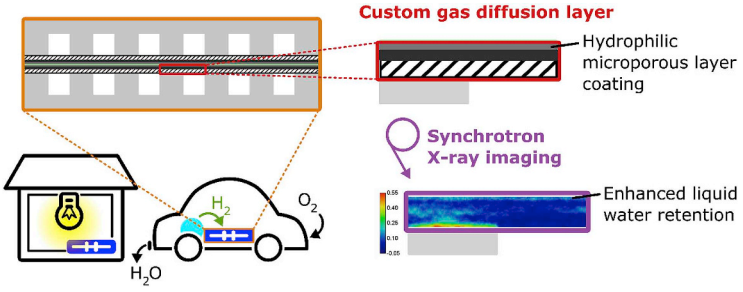
Pranay Shrestha, Rupak Banerjee, Jongmin Lee, Nan Ge, Daniel Muirhead, Hang Liu, Andrew Kai Cheung Wong, David Ouellette, Benzhong Zhao, Aimy Bazylak*

Thermofluids for Energy and Advanced Materials Laboratory, Department of Mechanical & Industrial Engineering, Institute for Sustainable Energy, Faculty of Applied Science and Engineering, University of Toronto, Toronto, Ontario, Canada

HIGHLIGHTS

- A hydrophilic MPL coating was applied to a commercial hydrophobic GDL.
- Membrane resistance decreased for the fuel cell without anode humidification.
- Liquid water retention increased at the catalyst layer-MPL interfaces.
- Liquid water accumulation within the cathode GDL increased at high current densities.
- Oxygen transport resistances increased at high current densities.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Polymer electrolyte membrane fuel cell
Gas diffusion layer
Microporous layer
Hydrophilic coating
Synchrotron X-ray radiographic imaging
No external humidifier

ABSTRACT

In this study, a hydrophilic microporous layer (MPL) coating was applied to a commercial hydrophobic bi-layer gas diffusion layer (GDL). We investigated the effect of the hydrophilic MPL coating on membrane hydration and liquid water distribution within the GDLs during fuel cell operation without anode humidification, using fuel cell performance monitoring and simultaneous synchrotron X-ray visualization. The application of the hydrophilic coating was found to enhance performance of the fuel cell. Specifically, the application of the hydrophilic MPL coating led to an increase in cell potential of up to 14% (0.07 V at 1.5 A/cm^2) and a decrease in fuel cell membrane resistance. The decrease in membrane resistance was attributed to improved membrane hydration. This improvement in membrane hydration was caused by the increase in liquid water retention at the catalyst layer-MPL interfaces. At high current densities, the application of the hydrophilic MPL coating led to increased liquid water accumulation within the cathode GDL, which subsequently led to increased oxygen transport resistance. Our study demonstrates that the wettability of the GDL can be tailored to enhance fuel cell performance for a desired range of operating conditions by balancing membrane hydration and oxygen transport.

Abbreviations: CCM, Catalyst coated membrane; Cryo-SEM, Cryo-scanning electron microscopy; EIS, Electrochemical impedance spectroscopy; GDL, Gas diffusion layer; MEA, Membrane electrode assembly; Micro-CT, Micro-computed tomography; MPL, Microporous layer; PEM, Polymer electrolyte membrane; RH, Relative humidity; Wt., Weight

* Corresponding author. Mechanical & Industrial Engineering, Faculty of Applied Science & Engineering, University of Toronto, 5 King's College Road, Toronto, ON, M5S 3G8, Canada.

E-mail address: abazylak@mie.utoronto.ca (A. Bazylak).

https://doi.org/10.1016/j.jpowsour.2018.08.062
Received 17 May 2018; Received in revised form 8 August 2018; Accepted 21 August 2018
0378-7753/

Nomenclature

Variables

C_A	Anode electric double layer capacitance [F/cm^2]
C_C	Cathode electric double layer capacitance [F/cm^2]
D_{eff}	Effective diffusion coefficient [m^2/s]
I	X-ray irradiance transmitted through sample
I_0	Incident X-ray irradiance
j	Unit imaginary number, $\sqrt{-1}$
L_y	Gas diffusion layer (GDL) thickness [m]
L_z	Length of the GDL parallel to the beam path [cm] ($L_z = 0.\ 80\ cm$)
N_t	Number of frames over time
N_x	Number of pixels in x-direction
R_A	Anode activation resistance [Ω·cm^2]
R_P	Cathode charge transport resistance [Ω·cm^2]
R_{mt}	Mass transport resistance of oxygen within the cathode [Ω·cm^2]
R_Ω	Ohmic resistance [Ω·cm^2]
$s_w(y)$	Liquid water saturation profile in the through-plane y-direction
$\bar{s}_{w,ave}$	Average liquid water saturation in regions of interest
t	Distance of propagation of beam within material [cm]
$t_{w,n}$	Normalized liquid water thickness [cm/cm$_{GDL}$]
$\bar{t}_{w,n}(y)$	Normalized liquid water thickness profile, averaged in x-direction and time [cm/cm$_{GDL}$]
Z_A	Impedance of the anode electrochemical reaction [Ω·cm^2]
Z_C	Cathode impedance [Ω·cm^2]
Z_{Tot}	Total impedance of the equivalent circuit [Ω·cm^2]
Z_W	Cathode Warburg impedance [Ω·cm^2]
Z_Ω	Ohmic impedance [Ω·cm^2]

Greek characters

$\varepsilon(y)$	Porosity profile of GDL in the through-plane y-direction
μ	Attenuation coefficient [cm^{-1}]
τ	Characteristic diffusive time of oxygen [s]
ω	Frequency of the AC signal [rad/s]

Subscripts

w	Relating to liquid water
Ref	Relating to reference image (dry-state image)
Wet	Relating to wet-state image obtained during fuel cell tests

1. Introduction

Polymer electrolyte membrane (PEM) fuel cells are promising devices that complement renewable energy infrastructure by providing on-demand electrical power [1]. To achieve widespread adoption, the cost of PEM fuel cells needs to be competitive with alternative technologies. The fuel cell stack cost (2017) for an 80-kW system exceeded the target cost set by US Department of Energy by 13% [2]. A potential avenue for reducing fuel cell cost is through effective water management, which improves fuel cell power output and efficiency [3–18].

Water is generated as a by-product of the cathode reaction (oxygen reduction reaction) during the electrochemical conversion of stored chemical energy of hydrogen into usable electricity. Effective water management requires a balance between two competing phenomena. On one hand, the accumulation of excess liquid water inhibits the efficient transport of reactant gases to the catalyst layer reaction sites [19]. To prevent excess liquid water accumulation, the gas diffusion layer (GDL) (composed of carbon fiber substrate and microporous layer (MPL)) is traditionally hydrophobized with polytetrafluoroethylene (PTFE) [20–22]. On the other hand, sufficient water is needed to hydrate the membrane to maintain high protonic conductivity. To achieve this, external humidifiers are conventionally employed to humidify the reactant gases. Removing external humidifiers reduces fuel cell system cost, size and parasitic power demands [2,4]. For example, the direct cost reduction of removing an external humidifier from an 80-kW fuel cell system is estimated to be $1/kW [23], which is equivalent to 20% of the total cost reductions required to meet the target of $40/kW by 2020. In addition, decreasing parasitic power demand by removing humidifiers increases power output of the fuel cell and further reduces the cost of the system. However, fuel cells typically suffer from performance losses (due to increased ohmic resistance) upon removing (or reducing) external humidification [24–26]. For example, the net power output of fuel cell systems (tested with commercial membrane electrode assemblies (MEAs)) decreased by up to 17% when external humidification was removed [27]. To minimize performance losses in the absence of external humidification, researchers have proposed several self-humidification strategies, such as the recirculation of anode or cathode gases [28–31], active water management [32,33], and design of tailored GDLs [3–9]. In this study, we will focus on a GDL-design based self-humidification strategy.

Recent studies have shown that hydrophilic MPLs improved fuel cell performance with low inlet humidification [3–9]. For instance, Kitahara et al. [3–6] fabricated multi-layered MPLs and controlled the hydrophilicity of the cathode MPLs. They demonstrated that a 5 μm-thick hydrophilic MPL, situated between the catalyst layer and the adjacent hydrophobic MPL, enhanced the fuel cell performance under low cathode humidification. They hypothesized that the hydrophilic layer helped preserve the hydration state of the membrane and the adjacent hydrophobic layer served as a barrier for water removal by dry air. Tanuma et al. [7–9] showed that the fuel cell performance of a hydrophilic MPL, which consisted of an ionomer (Flemion®) and vapor grown carbon fiber, was less susceptible to changes in gas pressure and inlet humidification under high temperature operating conditions. Their findings suggest that the addition of a hydrophilic MPL helps preserve water content within the membrane during low humidity conditions. Ahn et al. [10] demonstrated that a cathode GDL substrate coated with a hydrophilic MPL, which consisted of an ionomer (Nafion®) and carbon black, enhanced the fuel cell performance at both the fully humidified and non-humidified conditions. Despite the demonstrated performance improvement, we need liquid water visualization studies to investigate and understand the physical mechanisms leading to these performance improvements. Liquid water within the GDL affects the fuel cell performance by influencing membrane hydration and the oxygen transport resistance within the fuel cell. Liquid water visualization studies provide insights that will aid the design of next-generation GDLs for fuel cells operating without external humidification.

Liquid water in GDLs that contain hydrophilic components has been visualized using neutron radiography [34,35] and cryo-scanning electron microscopy (cryo-SEM) [36]. For instance, Mukundan et al. [34] used neutron radiography to show that the hydrophilic alumosilicate fibers in the MPL wicked liquid water away from the cathode catalyst layer, which led to decreased oxygen transport resistance. Aoyama et al. [36] used cryo-SEM to visualize the water (frozen immediately after fuel cell operation) in the cross-sections of two MEAs, one containing a hydrophilic MPL and the other containing a hydrophobic MPL. They reported the presence of larger quantities of ice in the pores of the hydrophilic MPL compared to the hydrophobic MPL, after fuel cell operation using fully humidified inlet gases. Forner-Cuenca et al. [35] patterned GDLs with longitudinal hydrophilic water removal pathways