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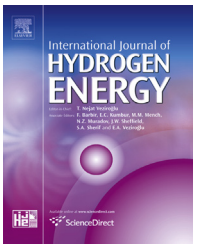

Influence of limiting throat and flow regime on oxygen bubble saturation of polymer electrolyte membrane electrolyzer porous transport layers

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ABSTRACT

In this work, the effect of porous transport layer (PTL) microstructure on the growth of oxygen gas bubbles was investigated using a microfluidic platform, termed PTL-on-Chip. The microfluidic chip was designed through stochastic pore network generation and height calibration, and was fabricated using soft-lithography. It was found that PTL throats have the dominating threshold capillary pressures compared to PTL pores; therefore, the size distribution of PTL throats ultimately govern the distribution of bubbles within the water saturated PTL. A unique throat is herein termed the *limiting throat*, whereby once it has been penetrated by the bubble, breakthrough instantly follows. This limiting throat is also the location of snap-off for subsequent bubble detachment. Within the porous media, oxygen bubble saturation increased as the distance of the limiting throat from the inlet increased. Lastly, it was observed that the heterogeneity of the PTL structure can enable the simultaneous co-existence of two flow regimes (capillary fingering and viscous fingering) at distinct regions within the bulk.

Introduction

Large energy storage is vital for harvesting renewable energy, such as wind and solar energy. The polymer electrolyte membrane (PEM) electrolyzer is a promising candidate for large scale energy storage in the form of hydrogen gas. Marked benefits of a PEM electrolyzer include capability of operating at high current densities (above 2 A/cm^2), producing pure hydrogen gas, and being installed as compact systems [1].

Fig. 1 is an illustration showing the working principles of a PEM electrolyzer. Liquid water is supplied to the anode catalyst layer (CL), where water is separated into protons, electrons, and oxygen. The protons are conducted through the

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Nomenclature

M	viscosity ratio
Ca	capillary number
$\mu_{injected}$	viscosity of the injected fluid, Pa·s
$\mu_{displaced}$	viscosity of the displaced fluid, Pa·s
Q	flow rate, m^3/s
A	Area, m^2
γ	surface tension, J/m^2
θ	contact angle, °
ε	porosity
r_{throat}	throat radius, m
a	minimum distance between two disks, m
b	network height, m
$r_{liquid\ channel}$	radius of channel, m
$\overline{r}_{throat}$	average radius of throats, m
$\overline{P}_{C,PTL}$	average capillary pressure of the PTL, Pa
$\nabla P_{channel}$	pressure gradient across the flow channel in a PEM electrolyzer, Pa/m
$\overline{d}_{PTL}$	average throat diameter of the PTL, m
$\overline{P}_{C,chip}$	average capillary pressure of the microfluidic network, Pa
$\nabla P_{chip\ channel}$	pressure gradient across the liquid channel in the PTL-on-Chip, Pa/m
$\overline{d}_{chip}$	average throat diameter of the microfluidic network, m
L	length of channel, m

solid polymer membrane, and the protons combine with the electrons that travel through an external circuit to form hydrogen gas at the cathode CL. The delivery of liquid water to the anode CL depends upon effective transport through the porous transport layer (PTL), which is also known as the gas diffusion layer (GDL) or porous current collector (CC).

The PTL, a porous substrate typically composed of titanium fibers or powders, is responsible for providing electron pathways to the active area and enabling the distribution of water to the CL. However, oxygen is a by-product of the electrochemical reaction that produces hydrogen, and oxygen bubbles resulting from this reaction often accumulate inside the pore space of the PTL. This accumulation of oxygen gas leads to reduced availability in surface area of the catalyst layer, blocked product and reactant diffusion pathways, and less effective thermal management within the electrolyzer [2]. Sun et al. [3] experimentally demonstrated that water starvation in the PEM electrolyzer can lead to a significant degradation in performance. Water starvation also led to the development of a heterogeneous voltage distribution, which could have subsequently led to localized hot spots and the accelerated degradation of electrolyzer materials [4]. Suermann et al. [5] showed that mass transport losses can contribute up to 25% of the total cell overpotential. Reducing the mass transport losses associated with oxygen bubble generation is critical for advancing the performance of PEM electrolyzers.

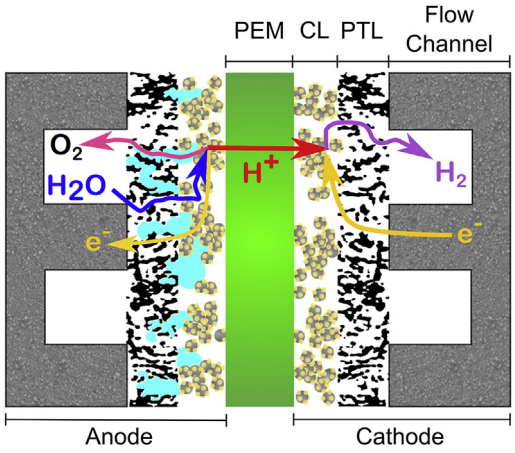

Fig. 1 – Illustration of a PEM electrolyzer cell.

The contributors to mass transport losses in PEM electrolyzers have not yet been fully characterized, due in part to the complexity of the microscale two-phase flow regimes in the PTL. As an alternative to studying the two-phase transport behavior inside the PTL, other authors have investigated the effect of the two-phase flow behavior of the flow channels on the distribution of reactants to the reaction sites [6,7]. Ito et al. [6] demonstrated that slug or annular flow of gas in the channel leads to increases in mass transport losses at high current densities. On the other hand, Dedigama et al. [7] experimentally observed that the transition of two-phase flow from bubbly to slug flow enhanced mass transport in an operating electrolyzer. Investigating two-phase flow behavior in a flow channel is a promising technique for studying the potential impacts of oxygen bubble accumulation in the channel on the water distribution in the PTL and delivery of water to the anode reaction sites. However, oxygen bubbles in the vicinity of the CL have a greater impact than those in the flow channel on the distribution of reactant water to the reaction sites. Understanding the influence of bubbles within the PTL is of great interest to improving effective mass transport in PEM electrolyzers.

The average pore size of typical PTLs is approximately 10 μm [8,9]; water and oxygen necessarily travel in counter-flow directions simultaneously through a confined space in order to achieve uninterrupted operation. Due to the competing transport mechanisms in the porous media, direct visualization provides an attractive means to understand the microscale multiphase flow behavior in PEM electrolyzers. Researchers have visualized PEM electrolyzers with techniques such as neutron radiography [10–12], synchrotron X-ray radiography [13] and low-energy X-rays [14]. Hoeh et al. [13] discovered that as the current density increased, the number of oxygen gas pathways increased, indicating that reducing mass transport losses becomes particularly important at high current density operation. Selamet et al. [14] demonstrated that oxygen gas accumulation was greater under the ribs of the flow channel, and they attributed this observation to the associated shorter electron pathway, which facilitates higher oxygen generation rates. Past visualization studies [10–15] have provided insights to the nature and impact of oxygen gas accumulation in PEM electrolyzers.

Also, previous parametric performance studies have shown that the structural properties of the PTL such as pore size, thickness, and fiber/powder size have a strong impact on cell performance [8,9,16–21]. Hwang et al. [16] showed that an increase in fiber size from 20 μm to 80 μm led to a reduction in

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