Electrochimica Acta 54 (2009) 6223–6233

Contents lists available at ScienceDirect

Electrochimica Acta

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

Engineering model for coupling wicks and electroosmotic pumps with proton exchange membrane fuel cells for active water management

Shawn Litster[1], Cullen R. Buie[2], Juan G. Santiago*

Department of Mechanical Engineering, Stanford University, Stanford, CA 94305, USA

ARTICLE INFO

Article history:
Received 3 December 2008
Received in revised form 15 April 2009
Accepted 5 May 2009
Available online 13 May 2009

Keywords:
PEM fuel cell
Water management
Wicks
Electroosmotic pump
Water pH

ABSTRACT

We present theoretical and experimental studies of an active water management system for proton exchange membrane (PEM) fuel cells that uses integrated wicks and electroosmotic (EO) pumps. The wicks and EO pumps act in concert to remove problematic excess liquid water from the fuel cell. In a previous paper, we showed that this system increases maximum power density by as much as 60% when operating with low air stoichiometric ratios and a parallel channel flow field. The theoretical model we develop here accounts for several key factors specific to optimizing system performance, including the wick's hydraulic resistance, the variation of water pH, and the EO pump's electrochemical reactions. We use this model to illustrate the favorable scaling of EO pumps with fuel cells for water management. In the experimental portion of this study, we prevent flooding by applying a constant voltage to the EO pump. We experimentally analyze the relationships between applied voltage, pump performance, and fuel cell performance. Further, we identify the minimum applied pump voltage necessary to prevent flooding. This study has wide applicability as it also identifies the relationship between active water removal rate and flooding prevention.

1. Introduction

Achieving proper water management in PEM fuel cells with perfluorosulfonic acid (PFSA) membranes (e.g., Nafion) without compromising system efficiency remains a significant technical impediment to commercialization [1]. Design and operation of fuel cells with these membranes requires careful consideration of the internal humidity. For example, a Nafion membrane in an 80% relative humidity environment has close to half the conductivity of the same membrane in a 100% relative humidity environment [2]. However, with high humidity levels, the oxygen reduction reaction at the cathode produces liquid water that inhibits reactant diffusion through the gas diffusion layers (GDLs) and catalyst layers and causes flow maldistribution in flow fields having multiple channels. A common strategy for minimizing liquid water flooding is to use a low number of serpentine channels in lieu of many parallel channels [3]. Employing serpentine channels increases local gas velocities and improves advective removal of water droplets. Similarly, high air flow rates improve water removal. However, both strategies increase the parasitic load associated with air pumping power, which is nominally the largest parasitic load on automotive fuel cell systems [4]. In addition, the use of high air stoichiometric ratio complicates system design because of the greater amount of water required to humidify the air.

There have been several unique passive [5,6] and active [7] approaches to water management, reviewed in Ref. [8]. Buie et al. [9] first demonstrated the removal of water from a PEM fuel cell using EO pumps. In that work, EO pumps were integrated within the channel walls of a single channel 1.2 cm^2 fuel cell. As Fig. 1a depicts, EO pumps generate flow when an electric field is applied across a porous glass substrate. EO flow is due to the coupling between an externally applied electric field and the charges of an electric double layer (EDL) which forms at the interface between liquids and solids. The applied electric field imposes a Columbic force on the diffuse layer of positive ions of the EDL and the motion of these charges drives a bulk flow through viscous interactions. In Litster et al. [8], we presented a new approach to water management using integrated wicking structures and an external EO pump to actively manage liquid water in PEM fuel cells.

Fig. 1b presents a cut-away schematic of the 25 cm^2 fuel cell with an integrated wick and external EO pump and illustrates the water removal pathway. Water produced within the membrane electrode assembly (MEA) is absorbed into the porous carbon wick and EO pump by capillary action. The porous carbon wick also serves as the air flow field "plate" and cathode current collector. The 0.5 mm thick

* Corresponding author at: Building 530, Room 225, 440 Escondido Mall, Stanford, CA 94305, USA. Tel.: +1 650 723 5689; fax: +1 650 723 7657.
E-mail addresses: litster@andrew.cmu.edu (S. Litster), crb@mit.edu (C.R. Buie), juan.santiago@stanford.edu (J.G. Santiago).
[1] Present address: Department of Mechanical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, USA.
[2] Present address: Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA.

0013-4686/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.electacta.2009.05.001

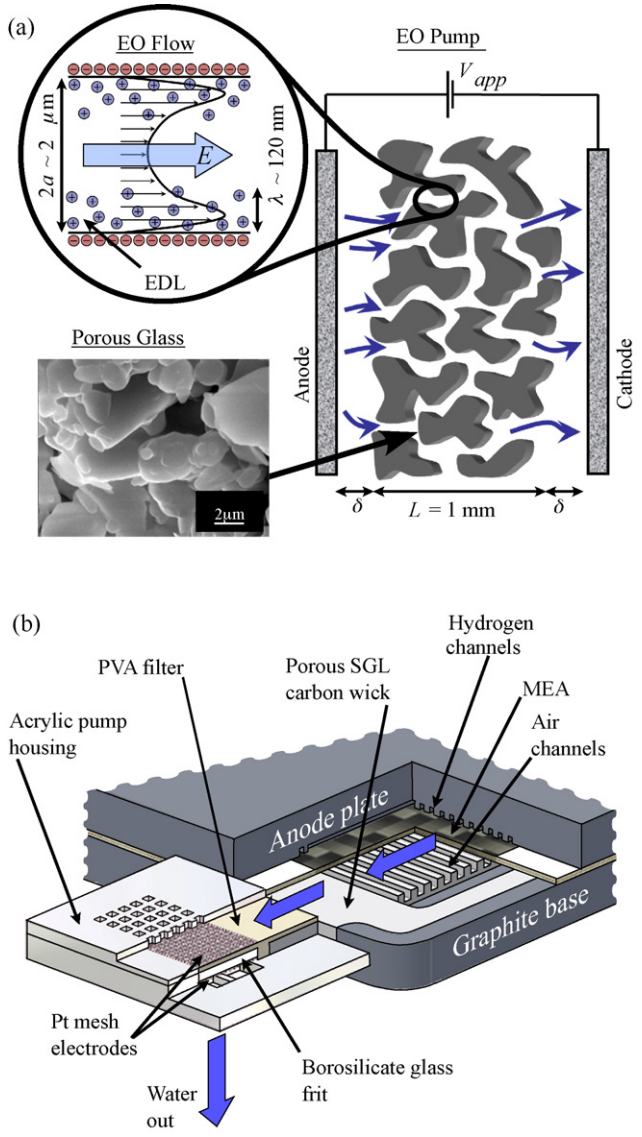

Fig. 1. (a) Schematic of EO flow in a porous glass EO pump. We form the EO pump by placing electrodes on either side of a porous glass substrate. The main schematic depicts flow through the porous glass substrate. A scanning electron micrograph (SEM) of the porous glass is shown in the bottom left. When saturated with water, the walls of the porous glass generate a negative charge and an EDL forms (schematic in upper left). The external electric field, E, imposes a Columbic force on the EDL's diffuse layer of positive charges and generates bulk flow by viscous interaction. (b) Cut-away schematic of the fuel cell assembly with an integrated porous carbon wick and an external 2 cm^2 EO pump. Water produced in the fuel cell's MEA wicks into the porous carbon until the wick and EO pump substrate are saturated. With a voltage applied across the mesh electrodes, the pump generates a local suction pressure in the wick that actively draws excess water from the cathode channels and GDL.

layer of porous carbon connecting the channel ribs allows liquid water to travel perpendicular to the channels rather than along the channels, which reduces the water's path length to the pump. The EO pump is coupled to the porous carbon via a polyvinyl alcohol (PVA) wick, which separates the electric currents of the fuel cell and EO pump. Once water saturates the porous borosilicate glass, the electric circuit between the platinum mesh electrodes of the EO pump is closed and the pump generates a suction pressure that pulls excess liquid water out of the fuel cell.

In Ref. [8], we demonstrated the ability of the wick and EO pump system to prevent flooding in a PEM fuel cell with a large number of parallel channels over a wide range of air stoichiometric ratios and current densities. The parasitic losses due to EO pumping were typically less than 0.5% of the fuel cell power. We gauged fuel cell performance enhancement with EO pumping by comparing this fuel cell's polarization curves with those of the fuel cell with the identical channel design and either no EO pumping or a non-porous flow field. At a low, efficient air stoichiometric ratio of 1.3, this system yielded a 60% increase in maximum power density. Strickland et al. [10] investigated the effect of active water management with EO pumps on the spatial distribution of current using a segmented anode plate.

In this paper, we provide a theoretical model to aid the design of these coupled devices and evaluate the scaling between EO pumps, wicks, and fuel cells. We present experimental results to support the theoretical model and investigate relationships between fuel cell performance and water removal rates. In this work, the EO pump operates with a constant applied voltage.

2. Theory

EO pumps are well suited to actively removing water from PEM fuel cells because of their small volume, low power requirement, and lack of moving parts. For a given application, the efficacy of pumping with electroosmosis depends on the four disparate length scales depicted in Fig. 1a. First, EO flow requires the presence of the nano-scale EDL at the interface between the liquid and the glass substrate. The EDLs of interest here have characteristic length scales of the order of 100 nm (consistent with water exposed to atmospheric air). Second, to generate adequate pressures with electroosmosis, the diameter of the pores must be sufficiently small to restrict the reverse flow generated by a pressure load (here our mean pore diameter is 2.0 μm). The third important length scale is the thickness of the pump substrate (here 1 mm). The average velocity in the pores depends on the local electric field and the local pressure gradient, which are both inversely proportional to pump thickness. The fourth length scale relates to the cross-sectional area of the EO pump because the flow rate is proportional to pump area (here we use a 2 cm by 1 cm pump).

Modeling a coupled fuel cell and EO pump system requires careful consideration of each of these physicochemical systems. Our present analysis is a significant extension of our previous work [9,11,12] in that we consider four additional factors: (1) the electrochemistry of pump electrodes; (2) the details of multi-dimensional water transport through the wick; (3) the effects of pressure-driven advective current in the pump (in addition to EO-driven advective and electromigration currents), and (4) the effects of EO pumping on pH and pump surface zeta potentials. In the next section, we summarize the key relation for pressure–load-specific flow rate from our previous work [9,11]. In the subsequent sections, we present the extensions listed above.

2.1. EO pumps: flow rate as a function of pressure load

To model EO pumps, we leverage the fact that the velocities of EO flow and the reverse, pressure-driven flow can be superposed linearly [13]. Yao and Santiago [11] modeled the flow rate, Q_{eo}, of a porous glass EO pump as flow through an array of cylindrical capillaries by accounting for the area, A_{eo}, porosity, ψ, and tortuosity, τ, of the porous pumping substrate. They provided the following relation for the flow rate, Q_{eo}:

$$Q_{eo} = A_{eo}\frac{\psi}{\tau}\left[-\frac{a^2}{8\mu_l}\frac{\Delta p}{L} - \frac{\varepsilon\zeta f}{\mu_l}\frac{V_{eff}}{L}\right] \quad (1)$$

where μ_l is the liquid viscosity, Δp is the pressure drop across the pump, L is the thickness of the substrate, ε is the liquid permittivity, and ζ is the zeta potential. The non-dimensional factor f accounts for the effect of the EDL's finite thickness on the velocity profile