Journal of Power Sources 268 (2014) 733–743

Contents lists available at ScienceDirect

Journal of Power Sources

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

Influence of membrane properties on the transient behavior of polymer electrolyte fuel cells

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HIGHLIGHTS

- Presents a detailed computational modeling of dynamic performance of PEM fuel cells.
- Analyzes the effects of membrane properties on the fuel cell performance and water management.
- Presents a novel graded design of membrane to prevent voltage reversals and dryout.

ARTICLE INFO

Article history:
Received 23 December 2013
Received in revised form
11 June 2014
Accepted 11 June 2014
Available online 18 June 2014

Keywords:
Polymer electrolyte membrane fuel cell
Computational modeling
Membrane hydration
Transient response
Graded membrane design
Membrane dryout

ABSTRACT

Understanding the performance of proton exchange membrane (PEM) fuel cells is critical to the water management in the fuel cell system. Low-humidity operating conditions present a complex interaction between dynamic behavior and water transport owing to different time scales of water transport mechanisms in the transient process. Toward understanding the effects of membrane properties on the dynamic behavior, this paper presents numerical simulations for a single channel PEM fuel cell undergoing changes in load, by subjecting the unit cell to step change in current. The complex interaction between cell voltage response and water transport dynamics for various membrane properties is explored in detail, where the performance is critically related to the water content of the membrane. Detailed computational fluid dynamics (CFD) simulations are carried out to show that step increase in current density leads to anode dryout due to electro-osmotic drag, and to investigate the dependence of transient behavior on the variations in membrane properties. The results show that water uptake by the membrane is a crucial factor in determining the occurrence of anode dryout and hence voltage reversal, and can be avoided by a graded membrane design.

1. Introduction

Proton exchange membrane (PEM) fuel cells offer much potential as energy efficient, clean and quiet, energy conversion devices for mobile and stationary applications. Due to major improvements in catalyst loading and membrane technology, PEM fuel cells have seen increased usage in various applications. A further reduction in cost can be achieved through better design and improved performance and durability of the fuel cells. This objective has generated much interest for research in control and optimization of transport and electrochemical processes in fuel cells [1,2]. While most of the research has been focused on steady-state operation, use of PEM fuel cells for automotive applications, where there are rapid changes in load, presents a need for better understanding of their transient behavior.

A PEM fuel cell is composed of membrane electrode assembly (MEA), sandwiched between porous gas diffusion layers (GDL) on either side, and bipolar plates with grooved-in gas channels of serpentine or interdigitated configurations. Humidified hydrogen (H_2) and oxygen (O_2) or air are transported, through anode and cathode flow channels, respectively, and are flowed through diffusion layers to react at the catalyst layers of the MEA. Hydrogen dissociates at the anode catalyst to produce protons that are transported across the thickness of the membrane to the cathode catalyst later where it combines with oxygen and electrons, flowing through an external circuit from the anode catalyst layer to the cathode catalyst layer, to produce water.

The performance of a fuel cell is critically related to the membrane hydration, as it affects the proton conductivity through membrane—a higher water content (number of water molecules per sulfonic acid group) in the membrane ensures higher

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http://dx.doi.org/10.1016/j.jpowsour.2014.06.065
0378-7753/

conductivity. Under low-humidity operation, suitable for automotive applications, electro-osmotic drag, back-water diffusion and rate of water supply or removal through humidified reactants, each associated with different time scales, interact in complex ways to affect the transient behavior of PEM fuel cells. The step increase in current density causes the anode side of the membrane to quickly dryout owing to electro-osmotic drag whereas back-diffusion of water from cathode to anode takes longer to rehydrate the membrane. This can lead to temporary dryout and hence sharp voltage drop, owing to jump in membrane resistance. As the back-diffusion rehydrates the anode side, the voltage recovers, improving the performance. The above transient behavior is strongly dependent on the transport and physical properties of the membrane namely, the water diffusion coefficient, electro-osmotic drag coefficient, thickness and equivalent weight, and needs to be studied in detail. Understanding the transient behavior and effect of membrane properties is of paramount importance for PEM fuel cells to be successfully deployed for mobile applications [1,2].

Several researchers have attempted to study the transient behavior of PEM fuel cells experimentally and numerically [3–14]. Hamelin et al. [3] studied the behavior and performance of a proton exchange membrane fuel cell stack for fast load commutations, observing that the system response was faster than 0.15 s. Kim et al. [4,5] investigated the effects of stoichiometry, reservoir and fuel dilution on the transient response of fuel cell, and elucidated the undershoot and overshoot characteristics for change in loads at fixed flow rate. Benziger et al. [6] studied the dynamic response of a stirred tank reactor (STR) PEM fuel cell for changes in load, emphasizing the role of membrane water uptake in ignition and extinguished state of the fuel cell. Yan et al. [7], in their experiments, investigated the steady state and dynamic performance of PEM fuel cells. The results showed cathode humidity, stoichiometric flow ratio and cell temperature as key parameters affecting the performance and being related to the water transport. The above studies point the importance of water transport and membrane hydration in the performance and transient response of fuel cells.

The transient response of fuel cells has been investigated numerically in several studies. The model by Um et al. [8] assumed constant water content and investigated the transient response of fuel cell, emphasizing the effects of reactant diffusion. Amphlett et al. [9] developed a lumped-parameter based thermal model to predict the transient response, while using steady-state electrochemical kinetics. Pathapati et al. [10] and Xue et al. [11] developed simplified system level models for their transient study. Ceraolo [12] used a simplified one-dimensional model to study the dynamic behavior, considering only the cathode side. These numerical studies used simplified models and lacked detail representation of complex interactions during transient operations. A more complete model was developed by Wang and Wang [13,14], extending the model used in Ref. [8] to include the effects of water accumulation and electrochemical double layer discharge. The transient model explored the dynamic behavior for step change in humidity, voltage and current, emphasizing the different time scales characteristic to transport and electrochemical process. To the authors' knowledge, Wang and Wang [14] were the first to simulate the effects of step changes in current load. The effects of two different membrane thicknesses on the dynamic behavior were studied in detail. It was pointed out in their study that the increase in current density leads to drying of anode leading to sudden drop in voltage.

In the present study, computational fluid dynamics (CFD) simulations are carried out using the model developed in Ref. [14] to study the effect of step change in current density. Although the work by Wang and Wang [14] provides mathematically rigorous description of the governing physics, the transport properties vary extensively by orders of magnitude and their influence has not been addressed in detail in previous studies. Majsztrik [15] presented an elaborate compilation of the diffusivity values of water in Nafion and the experimental techniques used, with values spanning over three orders of magnitude, at a single temperature. Similarly, the variations in water uptake, electro-osmotic drag coefficient, ionic-conductivity of membrane have been presented in Refs. [16–18], respectively. The variations in the physical and transport properties of GDL and membrane play an important role in determining the transient behavior of membrane and are addressed in detail in the present study. The mathematical model used as the basis of the study is presented in Section 2 and the results are reported and discussed in Section 3.

2. Mathematical model

Fig. 1 shows a schematic view of the two-dimensional (2D) section of a single channel PEM fuel cell corresponding to the geometry of the model considered in this study. Bipolar plates, gas channels, gas diffusion layers and catalyst layers on anode and cathode sides of a membrane constitute the different regions for this study. A two-dimensional, single phase, transient, isothermal model, following the assumptions in Refs. [1,13,14], is used to simulate the fuel cell dynamics with the objective of accurately capturing the transient water content distribution in the membrane. Owing to the low Reynolds number of the flow in gas channels laminar flow is assumed. The model takes into consideration important transient processes such as gas transport, water accumulation, and electrochemical double layer discharge. A single-channel of the fuel cell forms the computational domain for this study. The equations governing the dynamics of fuel cell behavior are as follows [13,14,19]:

$$\text{Continuity}: \ \nabla\cdot\vec{u} = 0 \tag{1}$$

$$\text{Momentum}: \ \frac{1}{\varepsilon}\left[\frac{\partial\vec{u}}{\partial t} + \frac{1}{\varepsilon}\nabla\cdot(\vec{u}\,\vec{u})\right] = -\nabla\cdot\left(\frac{p}{\rho}\right) + \nabla\cdot\tau + S_u \tag{2}$$

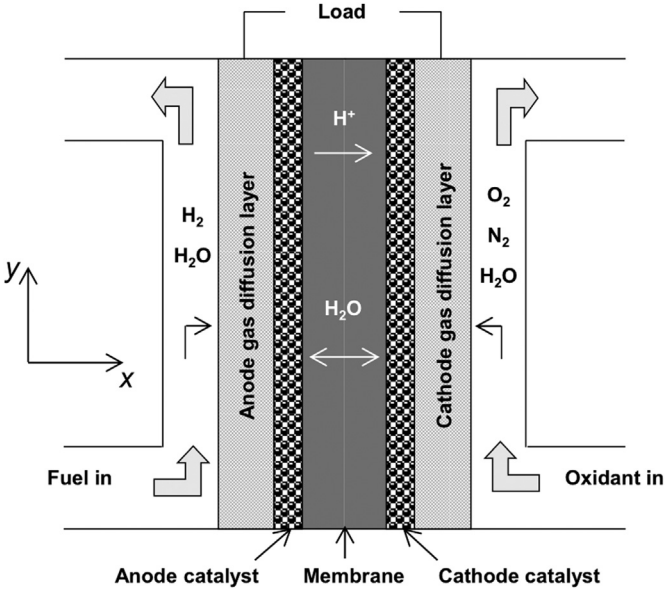

Fig. 1. Schematic view of the two-dimensional (2D) section of a single channel PEM fuel cell.