Journal of Power Sources 291 (2015) 46–57

Contents lists available at ScienceDirect

Journal of Power Sources

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

Design of a proton exchange membrane (PEM) fuel cell with variable catalyst loading

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HIGHLIGHTS

- Presents use of graded cathode catalyst layer to improve uniformity of local current density.
- Presents a computational analysis to determine optimum catalyst loading profiles.
- Experimentally demonstrates over 31% reduction in current density variation using graded cathode catalyst layer.

ARTICLE INFO

Article history:
Received 30 January 2015
Received in revised form
11 April 2015
Accepted 1 May 2015
Available online

Keywords:
Proton exchange membrane (PEM) fuel cell
Graded catalyst loading
Catalyst utilization
Current density distribution
Optimization

ABSTRACT

The performance and durability of proton exchange membrane (PEM) fuel cells is greatly affected by sharp temperature and stress gradients owing to the significant variation in local current density distribution. To improve the uniformity in local current density distribution and enhance the catalyst utilization, this paper proposes use of functionally graded catalyst loading in the cathode catalyst layer along the gas channel. A two-dimensional isothermal numerical model for PEM fuel cells combined with an optimization model was developed to determine the optimum cathode catalyst loadings and the associated local current density distributions for different operating conditions. Experiments were conducted to measure the local current density distribution for graded catalyst loading, using a segmented current collector. The results show that an optimized graded catalyst loading significantly reduces the current density variation along the length of the channel and enhances the catalyst utilization.

1. Introduction

The performance and durability of proton exchange membrane (PEM) fuel cells is greatly affected by the local current density distribution. Large variation in the local current density could exist along the channel leading to sharp local temperature and stress gradients causing the membrane electrode assembly (MEA) to degrade during operation [1–5]. The local current density, which is primarily determined by species transport and electrochemical reactions, is not uniform and decreases along the channel due to the concentration reduction of the reactant gases. Several studies have been reported to determine the local current density distribution in PEM fuel cells using *in situ* experimental techniques and numerical simulations [6–18], which point to drastic nonuniformity of 100% or more in the local current density variation.

The variation of the local current density may be made uniform through tailoring of the electrochemical reactions that occur along the fuel cell. One such approach is the use of a variable porosity gas diffusion layer (GDL) on the cathode side, as considered by Zhang et al. [19]. The study demonstrated that use of a graded porosity GDL, such that the porosity increased from the inlet to the outlet on the cathode side, led to an even distribution of the species within the catalyst, thereby improving uniformity of current density. In a similar approach, it is envisioned that large variations in the current density could be mitigated via tailoring the electrochemical reactions through appropriately designed catalyst layer and its composition such as, for example, functionally distributing the catalyst or electrolyte (e.g. Nafion). In fuel cells, the electrocatalytic reaction, apart from being a function of chemical composition and the electrochemical properties of the catalyst, also depends heavily

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http://dx.doi.org/10.1016/j.jpowsour.2015.05.002
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on the catalyst loading itself. A larger catalyst loading enables higher surface area for electrochemical reactions, thus involving more reactant species into the reactions, generating more current and decreasing the activation loss. The catalyst loading is more critical on the cathode side due to the significant activation polarization/kinetic loss for the oxygen reduction reaction (ORR). Thus, graded catalyst loading, especially at the cathode, controls the electrochemical ORR and the oxygen consumption, resulting in a uniform current density distribution. Furthermore, the high cost of the Platinum (Pt) catalyst requires improvements in the catalyst layer performance and catalyst utilization.

Several experimental and numerical studies have been performed to investigate the effect of catalyst layer composition on the performance of fuel cells. The optimum Nafion content in the catalyst layer was investigated in Refs. [20] and [21], while the effects of a cathode catalyst layer with graded Nafion content along the thickness of the layer were studied by Xie [22] and Wang et al. [23]. The influence of agglomerate size and ionomer distribution on reaction rate distribution and effectiveness of Pt catalyst utilization was investigated in Ref. [24]. Qi and Kaufman [25] experimentally investigated the effect of catalyst loading, Nafion content, cell temperature and electrode drying temperature on the power density of PEM fuel cells. It was found that maximum power density occurred for Nafion content of 30% and 0.20 ± 0.05 mg/cm^2 of platinum loading, also the maximum power density was found to increase linearly with increase cell temperature. The effects of design parameters in the catalyst layers such as Nafion content, Pt loading, thickness and porosity of catalyst layers on the cell performance were numerically studied by Song et al. [26] and Srinivasarao et al. [27]. Song et al. [26] used two-parameter optimizations to determine the best combination of two parameters (out of four) to maximize current density, whereas single parameter optimization was studied in Ref. [27]. The effects of catalyst loading on the PEM fuel cell performance were examined in Refs. [28–30], which showed that a low catalyst loading could be achieved using a treated novel membrane. Novel carbon aerogel supported Pt catalysts with varying pore size distributions and Pt content were synthesized and tested in Ref. [28].

Antoine et al. [31] and Ticianelli et al. [32] studied the effects of catalyst loading along the thickness of the cell. It was found that the optimal catalyst utilization occurs for a thin porous active layer and with Pt nanoparticles close to the proton exchange membrane side. Wilkinson and Pierre [33] investigated graded catalyst loading along the flow direction, suggesting enhanced performance for high catalyst loading at the inlet. Recently, Cetinbas et al. [34] numerically investigated the effects of bidirectionally-graded composition, with the catalyst loading variation along the thickness and in-plane direction, for cathode catalyst, and showed that a higher catalyst and/or ionomer loading at the membrane-catalyst layer interface improved the performance. Although the effects of localization of catalyst loading and Nafion content has been studied, the effects of catalyst loading on the localization of current production for variation in catalyst loading along the length has not been studied in detail and forms the scope of this study.

With the objective of improving the uniformity of current density distribution and enhancing catalyst utilization, this paper presents a systematic study on the design of functionally graded cathode catalyst loading. A two-dimensional isothermal numerical model is used to describe the transport phenomena and the electrochemical reactions inside a conventional PEM fuel cell. Variable catalyst loading at the cathode is parameterized using a power law functional form or a piecewise constant step variation along the channel. The computational model for the fuel cell is used with a numerical optimization based on the Nelder-Mead Simplex method to determine the optimum cathode catalyst loading variations that minimize the current density nonuniformity, for different operating conditions. Complementing the computational studies, experimental studies on membrane-electrode assemblies (MEAs) with graded cathode catalyst loading are also presented and compared with the numerical simulations.

The article is organized as follows: the mathematical model for a conventional PEM fuel cell is discussed in Section 2; the optimal design of the catalyst variation is described in Section 3; the experimental set up is presented in Section 4; and the optimization results from the numerical simulations and the experimental results are discussed in Section 5.

2. Mathematical model

Fig. 1 shows an illustration of a typical PEM fuel cell comprised of: (1) an anode current collector plate, with integrated fuel flow channels; (2) an anode gas diffusion layer (GDL); (3) an anode catalyst layer, where hydrogen oxidation reaction (HOR) takes place; (4) a proton exchange membrane; (5) a cathode catalyst layer for the ORR; (6) a cathode gas diffusion layer; and (7) a cathode current collector providing for oxygen gas transport. Hydrogen is fed into the channel and transported through the anode gas diffusion layer and arrives at the anode catalyst sites, where it dissociates into protons and electrons. Protons are transported with water inside the cell through the membrane to the cathode catalyst layer, while electrons are transported from the anode to cathode side through an external circuit. Oxygen (O_2) transported though the cathode gas diffusion layer to the cathode catalyst sites reacts with protons and electrons under the effect of catalyst and generates water.

The gas transport inside the cell is governed by the coupled continuity, momentum, and species conservation equations. The water transport from anode to cathode is modeled as source terms representing the osmotic drag, and is included in the momentum equations for the catalyst layers and the membrane. The electron transport is governed by solid phase potential equation in the catalyst and gas diffusion layers, while the proton transport is expressed as a membrane phase potential equation in the two catalyst layers and the membrane, in which the electrochemical reactions are represented as source terms based on the Butler–Volmer equation. The coupled governing equations presented here are formulated for the entire domain comprising of the seven regions described above for a two-dimensional cross section, with the thickness of the cell represented by x-direction and the length of the gas channel by y-direction, as depicted in Fig. 1. The unified formulation for an isothermal numerical model [1,19,35,36] is summarized as follows with specific source terms (Table 1) and the associated boundary conditions (Fig. 2):

$$\nabla\cdot\left(\rho\vec{V}\right) = S_C \tag{1}$$

$$\nabla\cdot\left(\rho\vec{V}\vec{V}\right) = -\nabla p + \nabla\cdot\boldsymbol{\tau} + S_V \tag{2}$$

$$\nabla\cdot\left(\rho\vec{V}y_i\right) = \nabla\cdot\left(\rho D_i^{eff}\nabla y_i\right) + S_i \tag{3}$$

$$\nabla\cdot\left(\sigma_j^{eff}\nabla\phi_j\right) + S_j = 0;\ j = s,\ m \tag{4}$$

where ρ is the fluid mixture density; $\vec{V}$ is the superficial velocity vector or average volume velocity vector; p is the pressure; $\boldsymbol{\tau}$ is the stress tensor; y_i represents mass fraction of i-th species; D_i^{eff} is the effective diffusivity of individual species; ϕ_j, $j = $ m, s represent the solid phase potential and the membrane phase potential