Uniform Reaction Rates and Optimal Porosity Design for Hydrogen Fuel Cells

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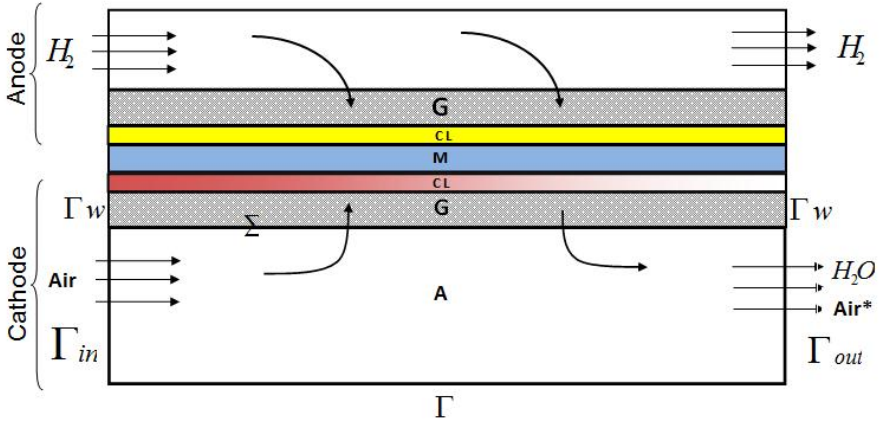
1. Introduction

Consider the **2d cross-section of hydrogen fuel cell** along the gas channels



Chemical reactions and Electricity production

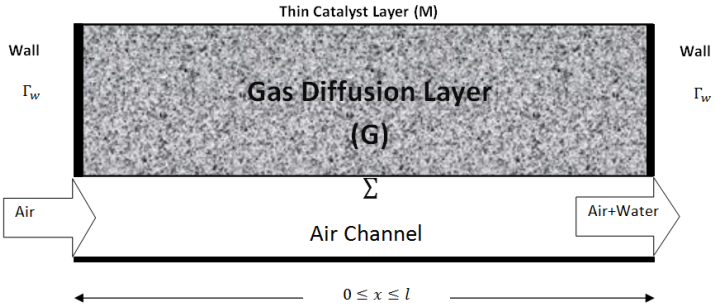
Anode: $2H_2 \longrightarrow 4H^+ + 4e^-$

Cathode: $4H^+ + 4e^- + O_2 \longrightarrow 2H_2O + \ Heat$

The electrons travel from the anode to the cathode through an external circuit generating electrical power.

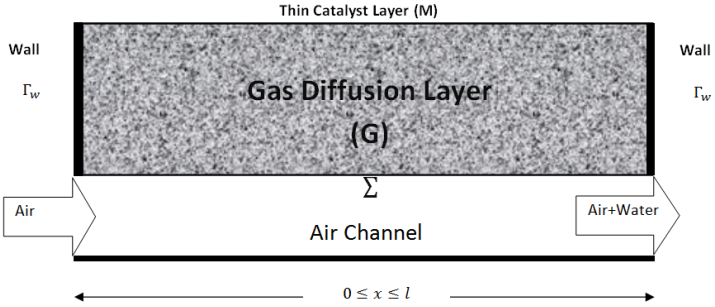
2. Literature Review

A gentle walk through literature review for fuel cells optimization:



- Kermani, et all: 2004, Novruzi, et all: Feb, 2004:
  reaction rate is not uniform on CL
- Novruzi, et all: Jul, 2004:
  water accumulation occurs where reaction is low
- Secanel, et all: 2007:
  maximizing the current density on the cathode CL by optimizing the platinum loading and gas diffusion layer porosity
- Secanel, et all: 2007-2010:
  optimizing the cathode and anode assembly to maximize the current density
- Mawardi, et all: 2005:
  optimizing the operating conditions to maximize the current density

- Song: 2004, et all:
  optimizing the cathode CL thickness to maximize the current density
- Grujicic: 2004, et all:
  optimizing the cathode dimensions and inlet pressure to maximize the current density



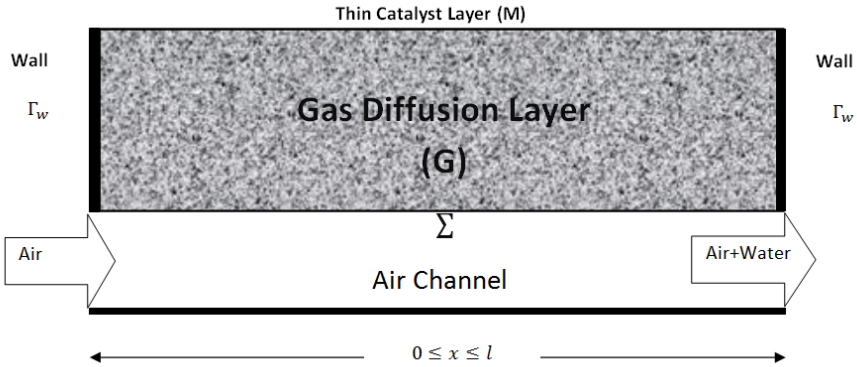
- Kumar: 2003, et all:
  testing rectangular, triangular and hemispherical cathode air channels to maximize the current density
- Jamekhorshid: 2011, et all:
  the importance of uniform current density
- Santis: 2006, et all:
  optimizing the catalyst loading to have the current density even on the cathode CL

2.1. Experimental Findings:

The current density or the reaction rate is not uniform on the cathode catalyst, which results in the following problems

- **drying out of the membrane** in regions with hight reaction rates
- **water accumulation** in regions with low water transport
- **non-optimum usage of the cathode catalyst**

3. Optimal Porosity Design of the GDL



Objective: to find an optimal porosity function $0.4 \le \varepsilon(x) \le 0.74$ that minimizes the efficiency cost functional

$$E(\varepsilon) := \int_M \left(\hat{c}(\varepsilon) - \overline{\hat{c}(\varepsilon)} \right)^2 dx, \tag{1}$$

subject to the state equations describing the fluid dynamics in the GDL. Here, a and b are given nonnegative parameters.
Take

$$\varepsilon(x) = \Sigma_{i=1}^{N} \varepsilon_i f_i(x), \quad 0.4 \le \varepsilon_i \le 0.8$$

3.1. Mathematical Modeling

Assumptions: steady state, isothermal, single gas phase

Let $\hat{c}_o$ (or simply $\hat{c}$), $\hat{c}_n$, $\hat{c}_w$ denote the mass fractions of oxygen, nitrogen and water vapor, and $\hat{\mathbf{u}}_g$, $\hat{p}_g$, ρ_g denote the velocity, the pressure and the density of the mixture.

3.1.1. In the GDL:

Using the method of volume averaging, the state of the system in G is modeled by

- **Conservation of total mass**

$$\nabla \cdot (\rho_g \hat{\mathbf{u}}_g) = 0, \tag{2}$$

  where $\hat{\mathbf{u}}_g$ is the superficial or extrinsic velocity.

- **Conservation of momentum** (Darcy equation)

$$\hat{\mathbf{u}}_g = -k(\varepsilon)\nabla \hat{p}_g, \tag{3}$$

  where $\hat{p}_g$ is the intrinsic pressure of the mixture, and $K(\varepsilon)$ is the permeability $K(\varepsilon)$ of the GDL divided by the dynamic viscosity μ of the mixture. Hence,

$$-\nabla \cdot (\rho_g k(\varepsilon)\nabla \hat{p}_g) = 0. \tag{4}$$

- Mass conservation of oxygen and nitrogen gives

$$\nabla \cdot N_o = \nabla \cdot (-D_o(\varepsilon)\rho_g \nabla \hat{c}_o + \rho_g \hat{c}_o \hat{\mathbf{u}}_g) = 0,$$

$$\nabla \cdot N_n = \nabla \cdot (-D_n(\varepsilon)\rho_g \nabla \hat{c}_n + \rho_g \hat{c}_n \hat{\mathbf{u}}_g) = 0,$$

  where $\hat{c}_o$ and $\hat{c}_n$ are the extrinsic mass fractions of oxygen and nitrogen, and $D(\varepsilon)$ is the effective diffusivity, which is a function of ε.

Previous Findings: the gas density ρ_g and the nitrogen mass fraction $\hat{c}_n$ can be assumed constant. This simplifies calculations as well.

3.2. GDL Mathematical Model

The physics in the GDL is the described by then"reduced" Darry low

$$-\nabla \cdot (k(\varepsilon)\nabla p_g) = 0$$

and the advection-diffusion equation for oxygen

$$\nabla \cdot (-D(\varepsilon)\nabla c + c\mathbf{u}) = 0,$$

where

$$\mathbf{u} = -k(\varepsilon)\nabla p_g.$$

3.2.1. Boundary Conditions:

- Let's assume that

$$p_g = p_\Sigma \text{ and } c = c_\Sigma$$

are both given on Σ.
- On the walls of the GDL,

$$u_1 = 0 \text{ and } N_o \cdot \nu = 0.$$

Since $u_1 = -k(\varepsilon)\partial_1 p_g$,

$$k(\varepsilon)\partial_1 p_g = 0 \text{ on } \Gamma_w$$

3.2.2. Catalytic Reaction:

• On the catalyst layer M, we have the Reaction Boundary Conditions:

$$\rho_g u_2 = N_o \cdot \nu + N_w \cdot \nu$$

$$\frac{1}{M_o} N_o \cdot \nu = \frac{-1}{2M_w} N_w \cdot \nu$$

$$2H^+ + \frac{1}{2} O_2 + 2e^- \rightarrow H_2O + \text{ Heat}$$

Also, the current density

$$i(x) = 4F \times \left(\frac{1}{M_o} N_o \cdot \nu \right)$$

and from Butler-Volmer equation

$$i(x) = \frac{2i_o c}{c_o^{ref}} \sinh \left(\frac{\alpha_c F}{RT} \eta \right)$$

Hence

$$N_o \cdot \nu = H_m c,$$

and

$$u_2 = -K(\varepsilon) \partial_2 p_g = -\beta_m c$$

3.3. Weak Formulation

Let q be a test function such that $q = 0$ on Σ. Then, the "reduced" Darcy is written as

$$\begin{aligned} 0 &= \int_G k(\varepsilon)\nabla p_g \cdot \nabla q - \int_{\partial g} (k(\varepsilon)\partial\nu p_g)q \\ &= \int_G k(\varepsilon)\nabla p_g \cdot \nabla q - \int_M (\beta_m c)q \end{aligned}$$

Find $p \in H^1_\Sigma(G)$ such that

$$\int_G k(\varepsilon)\nabla p \cdot \nabla q - \int_M (\beta_m c)q = 0, \text{for all } q \in H^1_\Sigma(G).$$

Similarly, a weak form for the advection-diffusion equation reads:

Find $c \in H^1_\Sigma(G)$ such that

$$\int_G [D(\varepsilon)\nabla \hat{c} - K(\varepsilon)\nabla p_g \cdot \hat{c}] \cdot \nabla\varphi + \int_M H_m \hat{c}\varphi = 0,$$

for all $\varphi \in H^1_\Sigma(G)$.

3.4. Porosity Optimization

Recall that

$$E(\varepsilon) := \int_M \left(c(\varepsilon) - \overline{c(\varepsilon)} \right)^2 dx,$$

and the optimal porosity

$$\varepsilon^* = (\varepsilon_1^*, \varepsilon_2^*, ..., \varepsilon_N^*)$$

is found by the Gradient Descent Method

$$\varepsilon_i^{n+1} = \varepsilon_i^n - \partial_{\varepsilon_i} E(\varepsilon^n),$$

where $\partial_i E(\varepsilon^n)$ requires $\partial_{\varepsilon_i} c$ for all $i = 1, 2, \ldots, N$.

But $\partial_{\varepsilon_i} c =: c'$ satisfies

$$\int_G k' \nabla p \cdot \nabla q + \int_G [D' \nabla c - k' \nabla p \cdot \nabla c] \cdot \nabla \varphi$$

$$+ \int_G k(\varepsilon) \nabla p' \cdot \nabla q - \int_M (\beta_m c') q$$

$$+ \int_G [D(\varepsilon) \nabla c' - k(\varepsilon) \nabla p' c - k(\varepsilon) \nabla p \cdot c'] \cdot \nabla \varphi$$

$$+ \int_M H_m c' \varphi = 0,$$

for all $\varphi, q \in H^1_\Sigma(G)$.

Remark: It is computationally very expensive to solve this system "N" times for each iteration.

3.5. Adjoint System

Now we choose particular $\varphi, q \in H^1_\Sigma(G)$ making the terms involving p' and c' equal to zero, integrate by parts and use $\partial_\nu \varphi = \partial_\nu q = 0$ on Γ_w :

$$\int_G k' \nabla p \cdot \nabla q + \int_G [D' \nabla c - k' \nabla p \cdot \nabla c] \cdot \nabla \varphi$$

$$- \int_G \nabla \cdot [k(\nabla q - \tilde{c} \nabla \varphi)] p' - \int_G [\nabla \cdot (D \nabla \varphi) + k \nabla \tilde{p} \cdot \nabla \varphi] c'$$

$$+ \int_M k(\partial_\nu q - \tilde{c} \partial_\nu \varphi) p' + \int_M (D \partial_\nu \varphi + H_m \varphi - \beta_m q) c' = 0$$

Since

$$\partial_{\varepsilon_i} E(\varepsilon) = \int_M g(\tilde{c}) c'$$

we set

$$D \partial_\nu \varphi + H_m \varphi - \beta_m q = -g(\tilde{c}) \text{ on } M.$$

Since also p' is unknown on M, we set

$$k(\partial_\nu q - \tilde{c} \partial_\nu \varphi) = 0 \text{ on } M.$$

The adjoint system defined as

I) $-\nabla \cdot (k\nabla q) = \nabla \cdot (\tilde{c}\nabla\varphi)$ in G

$\Sigma : q = 0, \qquad \Gamma_w : \partial_\nu q = 0$

$M : k(\partial_\nu q - \tilde{c}\partial_\nu \varphi) = 0$

Coupled with

II) $\nabla \cdot (D\nabla\varphi) - k\nabla\tilde{p} \cdot \nabla\varphi = 0$

$\Sigma : \varphi = 0, \qquad \Gamma_w : \partial_\nu \varphi = 0$

$M : D\partial_\nu\varphi + H_m\varphi - \beta_m q = -g$

Then

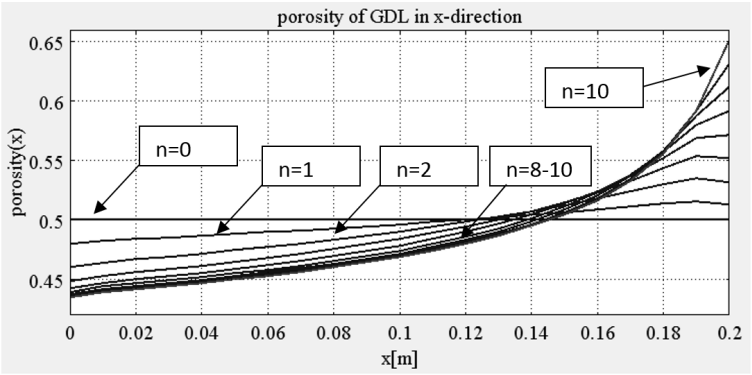
$$\begin{aligned}\partial_{\varepsilon_i} E(\varepsilon) &= \int_M gc' \\ &= \int_G [k'\nabla p \cdot \nabla q + (D'\nabla \tilde{c} - k'\nabla \tilde{p} \cdot \tilde{c})\nabla \varphi]\end{aligned}$$

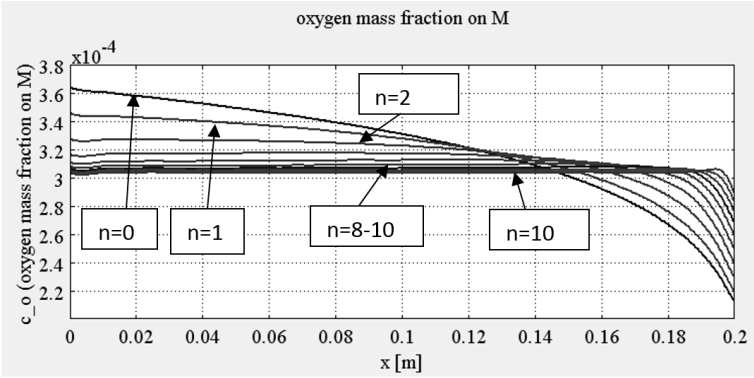
where $\tilde{c}, \tilde{p}$ are the solutions of the state equations, and φ, q are the solutions of the adjoint equations.

Remark: For each $\varepsilon-$ iteration, we only need to solve the state and adjoint equation to obtain on optimal porosity by means of

$$\varepsilon_i^{n+1} = \varepsilon_i^n - \partial_{\varepsilon_i} E(\varepsilon^n).$$

4. Numerical Results

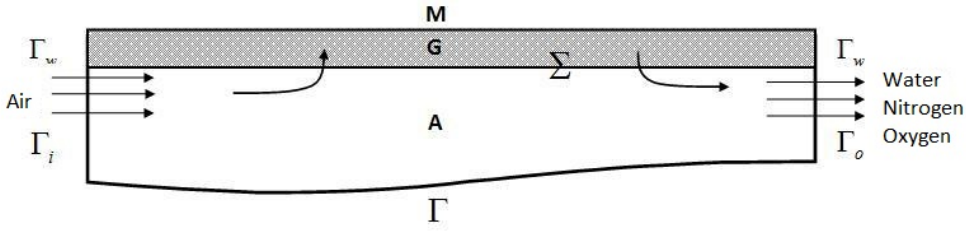




Thank You

4.1. Effect of the Geometric Design of Γ on the FC

Designing the shape of Γ so that
the **oxygen mass flux** $\mathbf{N_{o,y}}$ is as uniform and as large as possible on the catalyst layer (CL)
and the in/out **pressure drop** $\mathbf{p_{in} - p_{out}}$ along the channel as small as possible.



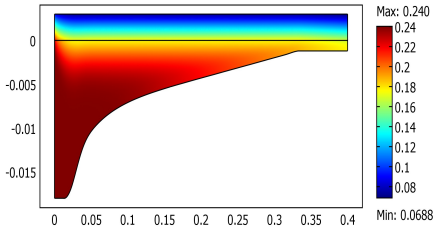
Or equivalently, find Γ that minimizes the following cost functional:

$$E(\Gamma) = \int_M \left(N_{o,y} - \frac{1}{M} \int_M N_{o,y} \right)^2 ,$$

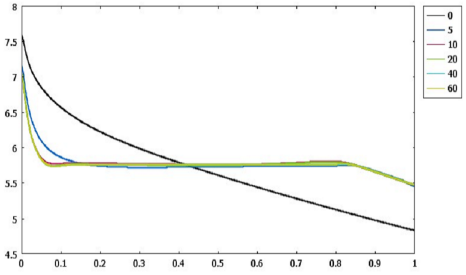
where a, b and e are some given nonnegative constants.

The variables $N_{o,y}$ and p_{in} are obtained through a **state problem** solved on A and G.

4.2. Optimal Design of the Air Channel



Oxygen mass fraction



Oxygen mass flux on the CL

This shape design of Γ improves the FC's efficiency as

- the catalyst layer is entirely used by the reactants
- accumulation of water and heat is reduced