



Optimal shape of catalyst loading along the oxygen channel of a PEM fuel cell

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ABSTRACT

A simple equation for the optimal shape of catalyst loading along the oxygen channel of a PEM fuel cell is derived. This shape $g(z; \lambda)$ is a one-parametric, independent of cell current function of the distance z along the channel; λ is the stoichiometry of the oxygen flow. Optimal g homogenizes local cell current not affecting the cell polarization curve.

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1. Introduction

Unless special measures are taken, the distribution of local current j_0 over the surface of a fuel cell is non-uniform. Various factors can contribute to this non-uniformity. To mention a few, these are inhomogeneities in feed molecules concentration, local temperature or local cell resistivity.

Inhomogeneity in j_0 is detrimental for stable long-term operation of a cell. Large local current is accompanied by the increase in local polarization voltage, in the electroosmotic flux of water through the membrane and in the local Joule heating. All these processes accelerate aging of cell components thereby lowering cell lifetime.

Most often inhomogeneity in j_0 is caused by uneven distribution of reactants. The reactants are usually distributed over the cell surface through a system of flow channels. Consider the cathode side of a PEM fuel cell. Oxygen molar concentration c decreases along the feed channel, since oxygen is consumed in the oxygen reduction reaction (ORR). The rate of ORR is proportional to c and hence j_0 is maximal at the inlet. Simple model shows that in the absence of flooding c and j_0 exponentially decrease with the distance z along the channel [1,2].

However, the rate of ORR is proportional to the local exchange current density as well. This value includes active surface of catalyst particles, which in turn is proportional to the catalyst loading. Is it

possible to compensate for the decay in oxygen concentration with the increasing along z catalyst loading?

Two works report the experimental study of the cells with non-uniform over the cell surface Pt loading on the cathode side. Santis et al. managed to significantly flatten the distribution of local current using the non-uniform Pt loading [3]. However, homogenization of j_0 was achieved at the cost of decreasing cell performance. Prasanna et al. showed that the non-uniform distribution of Pt enables to reduce total Pt loading not sacrificing the cell performance [4]. In both works various shapes of Pt loading growing toward the outlet of the oxygen channel were tested. It should be noted that these shapes were chosen in [3,4] rather arbitrarily; they did not follow from theory.

So far no attempts have been made to model the effect of in-plane variation of catalyst loading on cell performance.² To our best knowledge, all PEMFC models assume uniform catalyst loading over the cell surface (for review of PEMFC models see [5,6]).

In this work we derive a simple analytical expression for the optimal shape of catalyst loading along the oxygen channel. This shape appears to be a one-parametric function of the distance z , with the oxygen stoichiometry as a parameter. The model shows that the optimal shape of Pt loading homogenizes the local cell current, not affecting the cell polarization curve. Importantly, in the regime with fixed oxygen stoichiometry this optimal shape does not depend on the total cell current.

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² Experimental and theoretical studies of the effects due to catalyst gradient across the cathode catalyst layer were reported in [7,8]. However, here these effects are not considered and the through-plane shape of catalyst loading is assumed to be uniform.

2. Model

2.1. Polarization curve of the catalyst layer

Consider the cathode catalyst layer (CCL) of a PEM fuel cell. Note, however, that the calculations below are valid for any catalyst layer with Tafel kinetics of electrochemical reaction. Our main assumptions are:

- (1) Kinetics of electrochemical conversion are described by Tafel law.
- (2) Flow in the cathode channel is a well-mixed one with the constant velocity (plug flow).

For a moment we will assume that the transport loss of oxygen across the cell is negligible. However, below we will show that the account of this loss does not change the final result.

Following [9], the CCL performance is governed by equations:

$$\frac{\partial j(x)}{\partial x} = -i_* \left(\frac{c}{c_{\text{ref}}} \right) \exp \left(\frac{\eta}{b} \right) \quad (1)$$

$$j(x) = -\sigma_t \frac{\partial \eta(x)}{\partial x} \quad (2)$$

Here the axis x is directed from the membrane to the CCL/GDL interface (Fig. 1), $j(x)$ is the local proton current density, i_* is the volumetric exchange current density (a charge produced in unit volume per second, A cm^{-3}), c is the oxygen molar concentration, c_{ref} is the reference oxygen concentration, b is the Tafel slope, η is the local polarization voltage and σ_t is the proton conductivity of the CCL. Note that the catalyst loading appears in the system (1) and (2) as the factor i_* in Eq. (1).

Eq. (1) is proton current conservation equation. The right side of this equation is the Tafel rate of the ORR. Eq. (2) is Ohm's law relating proton current density with the gradient of overpotential.

We introduce the dimensionless variables

$$\tilde{x} = \frac{x}{l_t}, \quad \tilde{\eta} = \frac{\eta}{b}, \quad \tilde{j} = \frac{j l_t}{\sigma_t b} \quad (3)$$

where l_t is the CCL thickness. With these variables the system (1) and (2) takes the form

$$2\varepsilon^2 \frac{\partial \tilde{j}}{\partial \tilde{x}} = -\exp \tilde{\eta} \quad (4)$$

$$\tilde{j} = -\frac{\partial \tilde{\eta}}{\partial \tilde{x}} \quad (5)$$

where

$$\varepsilon = \frac{l_*}{l_t}, \quad (6)$$

and

$$l_* = \sqrt{\frac{\sigma_t b}{2i_*(c/c_{\text{ref}})}} \quad (7)$$

is the reaction penetration depth [10].

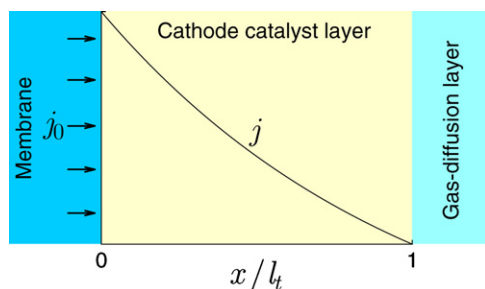


Fig. 1. Schematic of the cathode catalyst layer and the shape of proton current density j .

If current in the CCL is small ($j < \sqrt{2i_*\sigma_t b}$), in Eq. (4) we may set $\tilde{\eta} \approx \tilde{\eta}_0 = \text{const}$ and drop off Eq. (5). Solution to Eq. (4) shows that the proton current varies then linearly with \tilde{x} :

$$\tilde{j} = \frac{\exp \tilde{\eta}_0}{2\varepsilon^2} (1 - \tilde{x}) \quad (8)$$

Setting here $\tilde{x} = 0$ we get a low-current polarization curve of the CCL

$$2\varepsilon^2 \tilde{j}_0 = \exp \tilde{\eta}_0 \quad (9)$$

where $\tilde{j}_0 = \tilde{j}(\tilde{x} = 0)$ is the local cell current (Fig. 1).

If \tilde{j}_0 is large, the variation of polarization voltage across the CCL is no longer negligible. To obtain the high-current polarization curve we multiply Eqs. (4) and (5) together:

$$2\varepsilon^2 \tilde{j} \frac{\partial \tilde{j}}{\partial \tilde{x}} = \exp \tilde{\eta} \frac{\partial \tilde{\eta}}{\partial \tilde{x}}$$

and thus

$$\varepsilon^2 \frac{\partial (\tilde{j}^2)}{\partial \tilde{x}} = \frac{\partial (\exp \tilde{\eta})}{\partial \tilde{x}} \quad (10)$$

Integrating both sides we write $\varepsilon^2 \int_0^{\tilde{j}_0} d(\tilde{j}^2) = \int_{\tilde{\eta}_1}^{\tilde{\eta}_0} d(\exp \tilde{\eta})$, which yields

$$\varepsilon^2 \tilde{j}_0^2 = \exp \tilde{\eta}_0 - \exp \tilde{\eta}_1 \quad (11)$$

In the high-current regime the variation of $\tilde{\eta}$ along \tilde{x} is quite significant, so that $\exp \tilde{\eta}_1 \ll \exp \tilde{\eta}_0$ and Eq. (11) finally takes the form

$$\varepsilon \tilde{j}_0 = \exp \left(\frac{\tilde{\eta}_0}{2} \right) \quad (12)$$

2.2. Mass balance of oxygen along the channel

Oxygen mass balance in the cathode channel is

$$v^0 \frac{\partial c(z)}{\partial z} = -\frac{j_0(z)}{4Fh} \quad (13)$$

Here v^0 is the flow velocity, c is the oxygen molar concentration and h is the channel height.

Introducing dimensionless variables

$$\tilde{z} = \frac{z}{L}, \quad \tilde{c} = \frac{c}{c^0} \quad (14)$$

where L is the channel length and c^0 is the oxygen molar concentration at the inlet, we can rewrite Eq. (13) in the form

$$\lambda \tilde{j} \frac{\partial \tilde{c}}{\partial \tilde{z}} = -\tilde{j}_0 \quad (15)$$

where λ is the oxygen stoichiometry

$$\lambda = \frac{4Fh v^0 c^0}{LJ} \quad (16)$$

and J is the mean current density.

3. Optimal shape of catalyst loading

3.1. Low cell current

Eq. (15) with one of the polarization curves (9) or (12) determine the optimal shape of catalyst loading along the channel. In the equations above catalyst loading appears as the parameter i_* in the expression for ε (7). Let

$$i_* = \bar{i}_* g(\tilde{z}) \quad (17)$$

where \bar{i}_* is the mean exchange current density and $g(\bar{z})$ is a profile function, which describes the shape of catalyst loading along \bar{z} . In all cases the total amount of catalyst must be the same, that is

$$\int_0^1 g d\bar{z} = 1 \quad (18)$$

Substituting (17) into (7) we see that to rationalize the effect of g on cell performance, in the equations above the following replacement should be made

$$\varepsilon \rightarrow \frac{\varepsilon_0}{\sqrt{g(\bar{z}/\bar{c}_{\text{ref}})}} \quad (19)$$

Here

$$\varepsilon_0 = \sqrt{\frac{\sigma_t b}{2\bar{i}_* I_t^2}} \quad (20)$$

Consider first the low-current polarization curve Eq. (9). With the substitution (19) this equation takes the form

$$2\varepsilon_0^2 \bar{j}_0 = g \left(\frac{\bar{c}}{\bar{c}_{\text{ref}}} \right) \exp \bar{\eta}_0 \quad (21)$$

We will request, that the optimal shape of catalyst loading provides constant local current along the channel. Thus, optimal g is obtained from Eqs. (21) and (15) if we set $\bar{j}_0 = \bar{j}$. With this Eq. (15) takes the form

$$\lambda \frac{\partial \bar{c}}{\partial \bar{z}} = -1, \quad \bar{c}(0) = 1 \quad (22)$$

with the solution

$$\bar{c} = 1 - \frac{\bar{z}}{\lambda}. \quad (23)$$

Using this relation and setting $\bar{j}_0 = \bar{j}$, from (21) we get

$$2\varepsilon_0^2 \bar{j} = \frac{g}{\bar{c}_{\text{ref}}} \left(1 - \frac{\bar{z}}{\lambda} \right) \exp \bar{\eta}_0 \quad (24)$$

Solving this for g we obtain

$$g = \frac{2\varepsilon_0^2 \bar{c}_{\text{ref}} \bar{j} \exp(-\bar{\eta}_0)}{1 - (\bar{z}/\lambda)} \quad (25)$$

The function (25) must satisfy normalization condition (18). Integrating we get

$$\bar{j} = \frac{\exp(\bar{\eta}_0)}{2\varepsilon_0^2 \bar{c}_{\text{ref}} f_\lambda} \quad (26)$$

where

$$f_\lambda = -\lambda \ln \left(1 - \frac{1}{\lambda} \right) \quad (27)$$

Eq. (26) is the polarization curve of a cell with variable catalyst loading.³ Using (26) in (25) we finally find

$$g(\bar{z}) = \frac{1}{(1 - (\bar{z}/\lambda)) f_\lambda} \quad (28)$$

Remarkably, in the regime with constant λ the optimal shape of catalyst loading does not depend on mean current density \bar{j} .

³ We assume that the polarization voltage $\bar{\eta}_0$ is constant over the cell surface. The rationale for this assumption stems from the equation for cell voltage:

$$V_{\text{cell}} = V_{\text{oc}} - \eta_0 - R\bar{j}_0$$

If $\bar{j}_0 = \bar{j}$, then $\eta_0 = V_{\text{oc}} - V_{\text{cell}} - R\bar{j}$. Cell electrodes are usually equipotential, i.e., V_{cell} is constant along z . Assuming that the local cell resistivity R does not vary significantly along z we see that to a good approximation η_0 is also constant. Note that in the regimes with strong flooding variation of R with z is no longer negligible and the following relation holds: $\eta_0 + R\bar{j}_0 = \text{const}$.

3.2. High cell current

Plugging (19) into the high-current polarization curve (12), we get

$$\varepsilon_0 \bar{j}_0 = \sqrt{g \left(\frac{\bar{c}}{\bar{c}_{\text{ref}}} \right)} \exp \bar{\eta}_0 \quad (29)$$

Requesting again that the optimal loading provides constant local current along the cell we see that Eq. (23) remains unchanged and it should be substituted into Eq. (29) together with $\bar{j}_0 = \bar{j}$. This gives

$$\varepsilon_0 \bar{j} = \sqrt{\left(\frac{g}{\bar{c}_{\text{ref}}} \right) \left(1 - \frac{\bar{z}}{\lambda} \right)} \exp \bar{\eta}_0 \quad (30)$$

Solving this for g we find

$$g = \frac{\varepsilon_0^2 \bar{j}^2 \bar{c}_{\text{ref}} \exp(-\bar{\eta}_0)}{1 - (\bar{z}/\lambda)} \quad (31)$$

This result should obey the normalization condition (18); calculating integral we get the high-current polarization curve of a cell with variable catalyst loading:

$$\bar{j}^2 = \frac{\exp \bar{\eta}_0}{\varepsilon_0^2 \bar{c}_{\text{ref}} f_\lambda} \quad (32)$$

Substituting this into (31) we finally obtain

$$g(\bar{z}) = \frac{1}{(1 - (\bar{z}/\lambda)) f_\lambda} \quad (33)$$

This result coincides with the low-current shape Eq. (28).

The shapes (33) for several values of oxygen stoichiometry λ are depicted in Fig. 2. Qualitatively, the lower stoichiometry the faster oxygen consumption along \bar{z} and the faster should rise the catalyst loading with \bar{z} to compensate for the oxygen depletion. At high stoichiometries the function (33) tends to unity i.e., optimal loading is constant (Fig. 2).

3.3. The effect of transport loss in the GDL

Above we have neglected oxygen transport loss in the GDL. It is easy to show that the account for this loss does not change the main result of this work (33). Consider the low-current polarization curve (24). In the presence of transport loss in the GDL oxygen concentration in the catalyst layer \bar{c}_t is related to this concentration in the channel \bar{c} according to

$$\bar{c}_t = \bar{c} \left(1 - \frac{\bar{j}_0}{\bar{j}_D} \right) \quad (34)$$

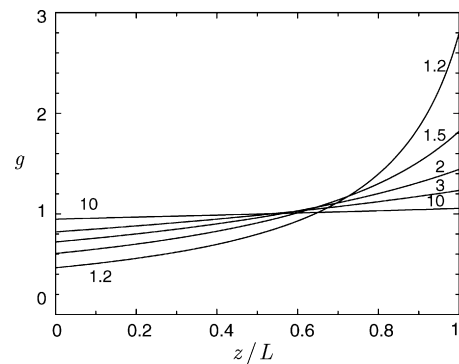


Fig. 2. Optimal shapes of catalyst loading (33) along the oxygen channel for indicated values of oxygen stoichiometry.

where j_D is the limiting current density due to oxygen transport through the cathode GDL [11].

Plugging (34) into (21), setting $\tilde{j}_0 = \tilde{j}$ and taking into account that $\tilde{c} = 1 - \tilde{z}/\lambda$, we get

$$g = \frac{2\varepsilon_0^2 \tilde{c}_{\text{ref}} \tilde{j}}{(1 - (\tilde{z}/\lambda))(1 - (\tilde{j}/\tilde{j}_D)) \exp(\tilde{\eta}_0)} \quad (35)$$

This result differs from (25) by a constant factor $1 - \tilde{j}/\tilde{j}_D$ in denominator. After normalization (18) this factor vanishes and we again come to (28). Similar procedure for the high-current regime leads to (33).

Thus, oxygen transport across the GDL does not affect the optimal shape of catalyst loading. Physically, this shape is determined by the profile of oxygen concentration along the channel (23), which is the same regardless of the through-plane transport loss in the cell.

3.4. Comparison of polarization curves

It is advisable to compare polarization curves of the cell with even and uneven catalyst distribution. Consider first the low-current regime; the polarization curve of a cell with uniform catalyst loading can be obtained from Eqs. (21) and (15). Setting in Eq. (21) $g = 1$, solving it for \tilde{j}_0 and using the resulting expression in Eq. (15), we get equation for \tilde{c} :

$$\lambda \tilde{j} \frac{\partial \tilde{c}}{\partial \tilde{z}} = -\frac{\exp \tilde{\eta}_0}{2\varepsilon_0^2} \left(\frac{\tilde{c}}{\tilde{c}_{\text{ref}}} \right), \quad \tilde{c}(0) = 1 \quad (36)$$

Solution to this equation is exponential function:

$$\tilde{c} = \exp \left(-\frac{\tilde{z}}{\tilde{z}_*} \right) \quad (37)$$

where

$$\tilde{z}_* = \frac{2\varepsilon_0^2 \tilde{c}_{\text{ref}} \lambda \tilde{j}}{\exp \tilde{\eta}_0} \quad (38)$$

Using (37) in (21) we see that \tilde{j}_0 varies along \tilde{z} also exponentially:

$$\tilde{j}_0(\tilde{z}) = \left(\frac{\exp \tilde{\eta}_0}{2\varepsilon_0^2 \tilde{c}_{\text{ref}}} \right) \exp \left(-\frac{\tilde{z}}{\tilde{z}_*} \right) \quad (39)$$

Local current must obey the following relation: $\int_0^1 \tilde{j}_0 d\tilde{z} = \tilde{j}$. Integrating (39) and equating the result to \tilde{j} we get the cell polarization curve

$$\tilde{j} = \frac{\exp(\tilde{\eta}_0)}{2\varepsilon_0^2 \tilde{c}_{\text{ref}} \lambda} \quad (40)$$

This equation coincides with Eq. (26). The same is true for the high-current regime: the polarization curve of cells with constant and variable catalyst loading are the same.

Thus, the shaping (33) does not change the cell performance; however, it homogenizes local current density. To illustrate the effect of current homogenization consider the cell with non-uniform loading and compare local current at the inlet $\tilde{j}_0(0)$ with the mean current density \tilde{j} . Setting in (39) $\tilde{z} = 0$ and dividing the result by (40) we get

$$\frac{\tilde{j}_0(0)}{\tilde{j}} = f_\lambda \quad (41)$$

The function f_λ tends to infinity as $\lambda \rightarrow 1$ and it tends to 1 as $\lambda \rightarrow \infty$ (Fig. 3). For λ close to 1 the ratio $\tilde{j}_0(0)/\tilde{j}$ is large; thus, homogenization of local current by non-uniform catalyst loading protects the cell from large over-current at the channel inlet.

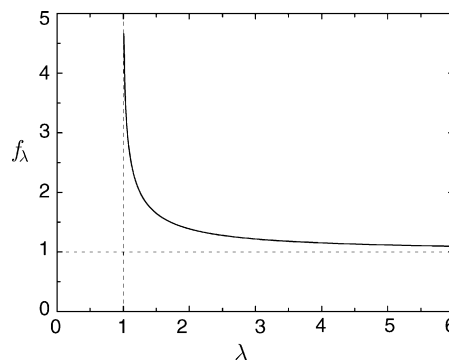


Fig. 3. The function $f_\lambda = -\lambda \ln(1 - (1/\lambda))$, which is the ratio of inlet local current density to the mean current density. At λ close to 1 this ratio is very large.

4. Discussion

The shape (28) was obtained assuming that the GDL is not flooded locally i.e., that the liquid water does not distort locally oxygen diffusion transport through the GDL.⁴ Severe local flooding may strongly distort the distribution of local current density in a cell and the shape (28) would no longer be optimal. Optimization of cell operation in the regime with strong local flooding requires special consideration. Note that the result of this work is applicable to high-temperature PEM fuel cells, which do not contain liquid water.

The shape (28) does not depend on cell current. This is the advantage of the regime with constant oxygen stoichiometry. In the regime with constant λ the profile of local current along z depends only on λ [1]. Therefore, one may expect that the shape of catalyst loading which homogenizes $j_0(z)$ also depends only on λ ; the model above confirms this idea.⁵

The effect of current homogenization due to optimal $g(z)$ may be particularly important in terms of cell aging. Large local over-current is usually accompanied by the increase in local half-cell polarization voltages on both sides of the cell. This may dramatically increase the rate of parasitic electrochemical processes (e.g. Ru dissolution in DMFC anode). Furthermore, local over-current may trigger propagation of the degradation wave in the cell [12]. All in all, homogenization of local current can increase the cell lifetime.

5. Conclusions

A simple equation for optimal distribution of Pt loading along the oxygen channel of a PEM fuel cell is derived. This equation is obtained assuming that the oxygen transport through the cathode catalyst layer is ideal, ORR kinetics obey Tafel law and the flow in the oxygen channel is a plug one.

The optimal shape of catalyst loading appears to be a one-parametric function of the distance along the oxygen channel with the stoichiometry of the oxygen flow λ as a parameter. In the regime with constant stoichiometry this shape does not depend on cell current. Optimal shape homogenizes local cell current not affecting the cell polarization curve. The closer λ to 1 the steeper the growth of optimal Pt loading toward the channel outlet. At infinite stoichiometry optimal is uniform loading.

⁴ Uniform flooding merely reduces the limiting current density \tilde{j}_D in Eq. (35). This parameter does not appear in the resulting expressions and hence uniform flooding does not affect the optimal $g(\tilde{z})$, Eq. (33).

⁵ In this work we do not discuss the method for preparation of MEA with the in-plane Pt gradient (see [4] for this method).

It is shown that the through-plane oxygen transport does not affect this optimal shape. The benefit of local current homogenization is discussed.

Appendix A. Nomenclature

\sim	marks dimensionless variables
b	Tafel slope (V)
c	oxygen molar concentration (mol cm^{-3})
c_{ref}	reference molar concentration (mol cm^{-3})
f_{λ}	dimensionless function of oxygen stoichiometry (27)
F	Faraday constant
g	dimensionless shape of the catalyst loading
j	local (through-plane) proton current density (A cm^{-2})
j_0	local (along the channel) current density of the cell (A cm^{-2})
i_*	local volumetric exchange current density (A cm^{-3})
\bar{i}_*	average volumetric exchange current density (A cm^{-3})
l_t	catalyst layer thickness (cm)
l_*	reaction penetration depth (cm), Eq. (7)
L	channel length (cm)
v^0	flow velocity in the cathode channel (cm s^{-1})
x	coordinate across the catalyst layer (cm)
z	coordinate along the channel (cm)

Subscripts

0	membrane surface (at $x = 0$)
1	catalyst layer/ GDL interface
t	catalyst layer

Superscripts

0	oxygen channel inlet (at $z = 0$)
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Greek letters

ε	l_*/l_t , dimensionless parameter (6)
ε_0	dimensionless parameter (20)
η	overpotential (V)
λ	stoichiometry of oxygen flow (16)
σ_t	proton conductivity of the catalyst layer ($\Omega^{-1} \text{cm}^{-1}$)

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