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# The effect of non–uniform aging of a polymer electrolyte fuel cell on the polarization curve: A modeling study

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ABSTRACT

Using the variational technique we show that in PEM fuel cells, an exponential shape of the local current density along the oxygen channel provides the best cell performance. A simple method for checking the quality of the local current density distribution by comparison of two polarization curves measured at different oxygen stoichiometries is suggested. Aging processes running non–uniformly along the channel distort the optimal shape of the local current and affect the cell polarization curve. Non–uniform aging of the cathode catalyst (agglomeration) increases the activation and transport overpotentials, not changing the limiting current density. Local lowering of the GDL oxygen diffusivity decreases the cell limiting current, not affecting the activation overpotential. A combined effect of the two aforementioned processes increases the slope of the polarization curve, which may be misinterpreted as the growth of the cell ohmic resistivity. An equation for reconstruction of the local current, exchange current density and GDL oxygen diffusivity shapes from the cell polarization curve is discussed.



## 1. Introduction

One of the key problems of a polymer electrolyte membrane (PEM) fuel cell technology is cell aging. Over the past decade, huge efforts have been directed toward understanding the mechanisms of cell aging and minimizing their effect on long–term cell performance [1,2].

In real applications, an active area of a PEM fuel cell is typically $10 \times 10$ cm$^2$ and the distribution of reactants over this area is usually non–uniform. To minimize the energy consumption by an air blower, PEM fuel cells and stacks operate at a relatively low stoichiometry of the oxygen flow $\lambda$. Typically, $\lambda$ is about 2, which means that the oxygen concentration at the channel outlet is twice less than at the inlet.

Non–uniformity of the oxygen concentration induces a non–uniformity in the distribution of local current over the cell surface, which, in turn, means non–uniform electrochemical and heat stresses. As a result, the cell aging is also non–uniform: the regions, where the local current is higher "die" faster. One of the most detrimental processes for the cell longevity is loss of the cathode catalyst active area due to Pt dissolution and agglomeration [3–5]. The results of the accelerated stress testing show that this process runs faster at the oxygen channel inlet, where the local current is larger [6].

Another reason for non–uniform current distribution over the cell surface is GDL flooding [7]. Numerous experimental and modeling studies show that liquid water tends to accumulate in the GDL close to the oxygen channel outlet [8–12]. Over time, hydrophobicity of the GDL decreases [2] and the GDL becomes prone to flooding. Flooding increases the local oxygen mass transport resistance, which lowers the local current and forces the non–flooded domain to produce larger current. Clearly, local GDL flooding and/or local loss of the catalyst active area affect the shape of the local current over the cell surface, thereby changing the cell polarization curve.

To study PEM fuel cells and stacks degradation, a number of accelerated stress tests (ASTs) have been suggested. AST protocols include potential cycling, high voltage hold, running the cell at open–circuit potential (OCP) and at variable relative humidity (RH) of inlet gases, cycled lowering of the oxygen stoichiometry etc. The results of ASTs of small–size cells have been interpreted using a 1D through–plane cell model; a qualitative agreement between the model and the detailed *in situ* and post–mortem experimental analyses has been demonstrated [13].

However, the aged polarization curves of the cells of an application–relevant size (active area ~50 cm$^2$ [14]) differ from the aged IV–curves of small–size cells with the active area ~1 cm$^2$ [13]. The experiments with the small–size cells have been deliberately performed under high oxygen and hydrogen stoichiometries, to minimize the non–uniformities over the cell surface

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| | |
|---|---|
| ~ | Marks dimensionless variables |
| $b$ | Tafel slope (V) |
| $c_h$ | Oxygen molar concentration in the channel (mol cm$^{-3}$) |
| $c_h^0$ | Oxygen concentration at the channel inlet (mol cm$^{-3}$) |
| $D_b$ | Oxygen diffusion coefficient in the GDL (cm$^2$ s$^{-1}$) |
| $F$ | Faraday constant |
| $f_\lambda$ | Dimensionless function, Eq.(13) |
| $J$ | Mean current density (A cm$^{-2}$) |
| $h$ | Channel depth (cm) |
| $J_{\rm lim}$ | Total limiting current density due to oxygen transport in the GDL (A cm$^{-2}$) |
| $j_h$ | Local cell current density (A cm$^{-2}$) |
| $j_{\rm lim}$ | Local limiting current density due to oxygen transport in the GDL (A cm$^{-2}$) |
| $j_{\rm lim}^0$ | Limiting current density, corresponding to the constant oxygen diffusivity along the channel (A cm$^{-2}$) |
| $i_*$ | Volumetric exchange current density of the ORR (A cm$^{-3}$) |
| $G$ | Total dimensionless catalyst loading in the CCL, Eq.(26) |
| $g$ | Dimensionless shape of the catalyst loading in the CCL |
| $L$ | Channel length (cm) |
| $l_b$ | GDL thickness (cm) |
| $l_t$ | Catalyst layer thickness (cm) |
| $q$ | Dimensionless shape of the oxygen diffusivity in the GDL |
| $V_{cell}$ | Cell potential (V) |
| $V_{oc}$ | Cell open–circuit potential (V) |
| $v^0$ | Flow velocity in the cathode channel (cm s$^{-1}$) |
| $z$ | Coordinate along the channel (cm) |

*Subscripts:*

| | |
|---|---|
| 0 | At the electrolyte/CL interface |
| 1 | At the CL/GDL interface |
| $b$ | In the GDL |
| $t$ | Catalyst layer |
| * | Characteristic value |

*Superscripts:*

| | |
|---|---|
| 0 | Channel inlet |

*Greek:*

| | |
|---|---|
| $\alpha$ | Dimensionless parameter in Eq.(33) |
| $\beta$ | Dimensionless parameter in Eq.(24) |
| $\eta_0$ | Total half–cell overpotential (V) |
| $\eta_{act}$ | Activation overpotential (V) |
| $\eta_{tra}$ | Transport overpotential (V) |
| $\Lambda$ | Functional to be maximized, Eq.(21) |
| $\varepsilon$ | Neman's dimensionless reaction penetration depth, Eq.(7) |
| $\lambda$ | Oxygen stoichiometry, Eq.(4) |
| $\sigma_t$ | CCL proton conductivity ($\Omega^{-1}$ cm$^{-1}$) |
| $\phi$ | Stream function, Eq.(18) |
| $\chi$ | Dimensionless parameter in Eq.(39) |

[13]. The resulting polarization curves of the aged cells exhibit a resistive–like behaviour in the range of low cell potentials. In contrast, the large–scale cells in [14] have seemingly been operated in standard conditions under relatively low oxygen stoichiometry,

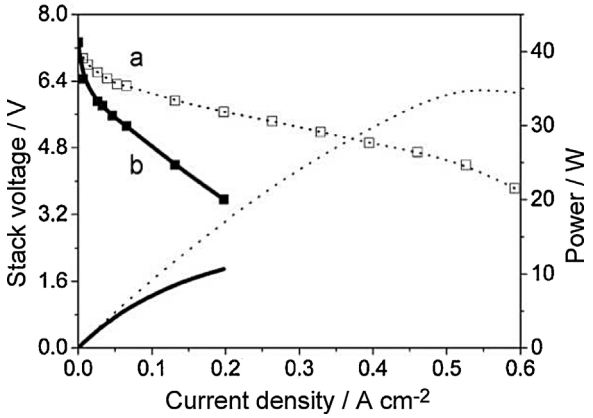


**Fig. 1.** (Reprinted from [5]). Polarization and power curves obtained at 0.8 atm backpressure for the PEMFC stack before (a, dotted line) and after (b, solid line) the AST (Accelerated Stress Testing). Operation conditions: H2/O2: 1.5/3.0; $T_{stack}$: 323 K.

and their "aged" polarization curves clearly exhibit mass–transport limiting current density.

Polarization curves of a PEMFC stack before and after the AST with several protocols (including operation at a relatively low oxygen stoichiometry and at a low RH of inlet gases) are shown in Figure 1 [5]. Though the mass–transport region has not been reported, the medium–current slope of the "aged" polarization curve dramatically increases (Figure 1). Below, we show that this shape can be explained by a combined effect of (i) non–uniform aging of the cathode catalyst due to Pt agglomeration and (ii) non–uniform worsening of the GDL transport properties [3].

In this work, we rationalize the effects of these two types of local non–uniformity on the cell polarization curve. We show that the non–uniform lowering of the GDL oxygen diffusivity (due to flooding) decreases the cell limiting current density, not affecting the polarization curve in the region of small currents. In contrast, non–uniform lowering of the exchange current density (due to catalyst agglomeration) reduces the cell performance at all currents. A combined effect of the aforementioned processes reduces the slope of the polarization curve in the whole range of currents, which may be misinterpreted as the growth of the cell resistance.

The goal of this work is to demonstrate the importance of studying *local* cell aging, when different domains of the cell active area experience different stressing factors. The structure of the paper is as following. We briefly discuss derivation of the local current density shape in the cell with uniform along the oxygen channel exchange current and oxygen transport properties. Using the Lagrange–Euler equation, we proof that this shape maximizes the limiting current density of the cell. We discuss a simple means for checking the local current distribution by using two polarization curves measured at different oxygen stoichiometries. Then we show how non–uniform distributions of the exchange current and of the local oxygen diffusivity in the GDL affect the cell polarization curve. We compare the polarization curves of a pristine and non–uniformly aged MEAs, corresponding to the different mechanisms of aging. Finally, we discuss an equation for the reconstruction of the local current, exchange current density and GDL oxygen diffusivity shapes from the cell polarization curve.

[3] Typically, GDL includes a microporous layer (MPL) located adjacent to the catalyst layer. The role of the MPL is to improve removal of excess water from the cathode catalyst layer (CCL). However, carbon corrosion of the MPL make this layer vulnerable to flooding, which is the main cause of the decay in the cell limiting current density [15].