

# The voltage current curve of a PEM fuel cell: Analytical and numerical modeling

A. Kulikovsky

Research Center “Juelich”, IWV-3  
D-52325 Juelich, Germany, A.Kulikovsky@fz-juelich.de

## ABSTRACT

The formulas for polarization voltage of the cathode catalyst layer of a PEM fuel cell are obtained. Based on these formulas, the fitting equation for the voltage current curve of a cell is constructed. The terms of this equation have clear physical meaning; the coefficients are expressed in terms of basic transport and kinetic parameters of a cell. The equation is then used to fit experimental voltage current curve and to estimate the parameters of the real cell. With this set of parameters a quasi-3D simulation of the cell is performed. Comparison of simulated, experimental and analytical voltage current curves allows to isolate the contribution of 2D effects to cell performance. This combination of analytical and numerical models enables to characterize membrane-electrode assemblies and flow fields using experimental voltage current curves.

**Keywords:** Voltage current curve, PEM fuel cell, modeling

## 1 INTRODUCTION

The voltage current curve is a main performance characteristic of a polymer electrolyte membrane (PEM) fuel cell. This curve summarizes voltage losses caused by many physical and electrochemical processes in a cell.

Due to excellent kinetics of hydrogen ionization, the main contribution to voltage loss usually is at the cathode side. Kinetic parameters of oxygen reduction reaction, transport of oxygen to the catalyst sites and proton conductivity of the active layer determine the quality of the membrane-electrode assembly (MEA). In real systems oxygen is usually supplied through the meander channels. The system of alternating channels and ribs is a source of 2D and 3D transport losses. Voltage loss depends also on the regime of cell operation, e.g. low humidification of feed gases translates to low membrane conductivity, which increases ohmic loss.

Since pioneering works [1,2], the fuel cell often is considered as the one-dimensional (1D) system, in which all fluxes are directed only across the cell. More sophisticated 2D and 3D models (see e.g. [3]–[5]) take into account non-uniformity of currents and feed gases concentration along- and across-the-channel.

Being valuable tool for understanding the physics of fuel cell operation in particular regimes, numerical model do not give trends. This is the task of analytical theory. On the other hand, numerical model can serve as an instrument for verification of the theory predictions.

This work aims to demonstrate that the combination of analytical and numerical modeling enables to estimate basic transport and kinetic parameters of the real fuel cell and to isolate the contribution of 2D effects to the overall cell performance. This approach is based on recently developed analytical and quasi-3D numerical models of a PEM fuel cell.

## 2 ANALYTICAL MODEL

Let the proton current density  $j_0$  comes to the catalyst layer from the membrane (Figure 1). We will

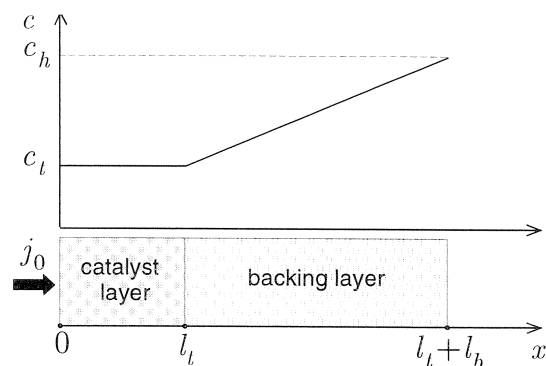


Figure 1: Sketch of the problem of the catalyst layers performance. Oxygen concentration varies linearly in the backing layer with the slope, determined by the current density  $j_0$ . In the catalyst layer oxygen concentration is assumed to be constant.

assume, that the oxygen concentration in the catalyst layer  $c_l$  is constant across the layer (validity of this approximation is discussed in [6]). The catalyst layer per-

formance then is described by equations

$$\frac{\partial j}{\partial x} = -i_* \left( \frac{c_t}{c_{ref}} \right)^\gamma \exp \left( \frac{\alpha F}{RT} \eta \right) \quad (1)$$

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

Equation (1) describes consumption of the proton current density  $j$  along  $x$  due to oxygen reduction reaction at a rate, given by the r.h.s.. Here  $c_t$  and  $c_{ref}$  are available in the catalyst layer and reference oxygen molar concentrations,  $i_*$  is volumetric exchange current density ( $\text{A cm}^{-3}$ ) and  $\alpha$  is transfer coefficient. Overpotential  $\eta = \varphi_m - \varphi$  substitutes in (2) membrane phase potential  $\varphi_m$ , since the carbon phase potential  $\varphi$  is assumed to be constant.

The exact solution of equations (1)–(2) leads to implicit relation of the catalyst layer polarization voltage  $\eta_0$  and  $j_0$  [7]. This relation is further extended in [6] to take into account oxygen transport in the backing layer (and thus to describe the effect of limiting current density). In the limiting cases of small and large current densities the following explicit formulas for  $\eta_0$  are obtained [6]:

$$\frac{\eta_0}{\eta_*} = \ln \left( \frac{j_0}{j_*} \right) - \ln k - \gamma \ln \left( 1 - \frac{j_0}{j_{lim}^D} \right), \quad j_0 \ll j_* \quad (3)$$

$$\frac{\eta_0}{\eta_*} = 2 \ln \left( \frac{j_0}{j_*} \right) - \ln k - \gamma \ln \left( 1 - \frac{j_0}{j_{lim}^D} \right), \quad j_0 \gg j_* \quad (4)$$

where

$$\eta_* = \frac{RT}{\alpha F}, \quad k = \frac{l_t i_*}{j_*} \left( \frac{c_t}{c_{ref}} \right)^\gamma, \quad j_{lim}^D = 4F \frac{D_b c_h}{l_b} \quad (5)$$

and

$$j_* = \frac{2\sigma_t \eta_*}{l_t}. \quad (6)$$

Here  $\eta_*$  is Tafel slope,  $j_{lim}^D$  is the limiting current density caused by imperfect oxygen transport through the backing layer,  $D_b$  is oxygen diffusion coefficient in the backing layer,  $l_b$  is backing layer thickness,  $c_h$  is the oxygen molar concentration in the feed channel,  $\sigma_t$  is proton conductivity of the catalyst layer and  $l_t$  is its thickness.

The first term on the right hand sides of (3) and (4) is the reaction activation overvoltage. The second term ( $\ln k$ ) describes the effects of exchange current density and concentration overpotential. The third term gives voltage loss due to oxygen transport in the backing layer.

The characteristic current density  $j_*$  (6) separates low- and high-current regimes of cell operation. In the high-current regime ( $j_0 \gg j_*$ ), the activation overvoltage is twice larger, than in the low-current regime ( $j_0 \ll j_*$ ). It is thus beneficial to increase  $j_*$  (i.e., to increase  $\sigma_t$  or to decrease  $l_t$ ) in order to maintain the cell in the low-current regime. Physically, in the

low-current regime local overpotential is almost constant across the catalyst layer and all parts of the layer equally contribute to the proton current consumption. In the high-current regime  $\eta(x)$  has a distinct peak at the membrane surface, that is higher overvoltage is required to consume the same current [7] (see also [8], [9]). This appears to be equivalent to twice larger Tafel slope.

Low- and high-current formulas can be combined in one using the function  $\phi(y) = 1 + \frac{y}{1+y}$ , which changes from 1 to 2 as its argument changes from small to large values. We then have

$$\frac{\eta_0}{\eta_*} = \phi \left( \frac{j_0}{j_*} \right) \ln \left( \frac{j_0}{j_*} \right) - \ln k - \gamma \ln \left( 1 - \frac{j_0}{j_{lim}^D} \right) \quad (7)$$

This equation approximately describes the transition region  $j_0 \simeq j_*$  and thus is valid for all  $j_0$ .

Cell voltage is

$$V_{cell} = V_{oc} - \eta_0 - \frac{j_0 l_m}{\sigma_m} \quad (8)$$

where  $V_{oc}$  is open circuit voltage and the last term takes into account ohmic losses in the membrane ( $l_m$  and  $\sigma_m$  is the thickness and proton conductivity of bulk membrane).

Relation (8) with  $\eta_0$  (7) may serve as the fitting equation for experimental voltage current curve. This equation contains four parameters  $\eta_*$ ,  $j_*$ ,  $k$  and  $j_{lim}^D$ ; all of them have clear physical meaning (if  $\sigma_m$  is not known, it should be included to the list of fitting parameters). Fitting the experimental voltage current curve and using the formulas (5), (6) one can estimate the basic kinetic and transport parameters of the cell.

This procedure was performed for PEM fuel cell designed at Paul Scherrer Institute (Switzerland). Conditions and fitting parameters are listed in Table 1. The

Conditions	
Cell temperature $T$ ( $^{\circ}\text{C}$ )	70
Pressure on both sides (atm)	2.2
Catalyst layer thickness $l_t$ ( $\mu\text{m}$ )	30
Backing layer thickness $l_b$ ( $\mu\text{m}$ )	200
Assumed parameters	
Proton conductivity of the catalyst layer $\sigma_t$ ( $\Omega^{-1} \text{cm}^{-1}$ )	0.01
Reference oxygen concentration $c_{ref}$ (mole $\text{cm}^{-3}$ )	$3.2 \times 10^{-5}$
Fitting parameters	
Transfer coefficient $\alpha$	0.65
Effective reaction order $\gamma$	1.2
Exchange current dens. $i_*$ ( $\text{A cm}^{-3}$ )	$1 \times 10^{-2}$
Oxygen diffusion coeff. $D_b$ ( $\text{cm}^2 \text{s}^{-1}$ )	$2.6 \times 10^{-3}$

Table 1: Conditions and parameters

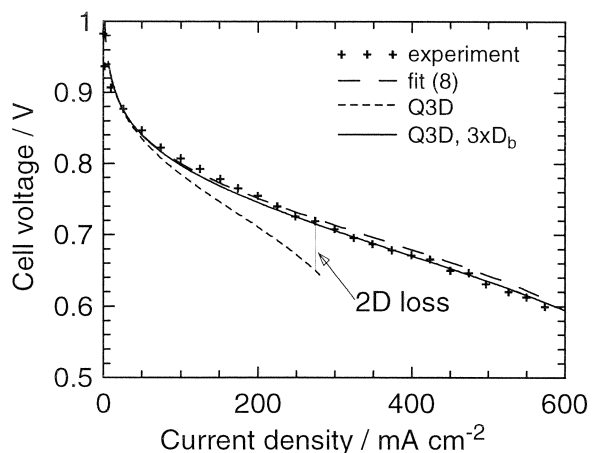


Figure 2: Experimental voltage current curve of the PEM fuel cell (dots), theoretical fit (8) (long-dashed line), the result of quasi-3D simulation with the parameters, obtained from the fit (short-dashed line) and the result of Q3D simulation with 3 times larger oxygen diffusion coefficient in the backing layer (solid line).

result is shown in Figure 2 (long-dashed line). Equations (8), (7) reasonably fit the experiment (dots). The coefficients of the fitting equation immediately give the estimate of parameters of the cathode side (Table 1, fitting parameters).

### 3 Q3D MODELING

Using parameters obtained from fitting, a quasi-3D simulation of this cell was performed. In brief, quasi-3D model gives the map of currents, feed gases concentration etc in a cell cross section (Figure 3), taking into account along-the-channel consumption of feed gases.

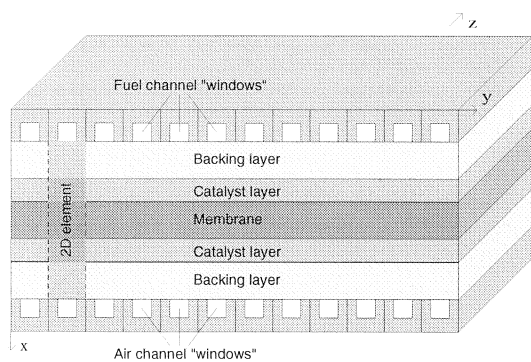


Figure 3: Sketch of the computational domain for Q3D model.

Model equations are formulated for single 2D element, shown in Figure 3. The model is based on mass

and current conservation equations, coupled by Butler-Volmer relations for the rates of electrochemical reactions. The model takes into account water transport through the membrane.

The cross section of a fuel cell, equipped with long meander channels consists of a number of 2D elements (Figure 3); these elements form the domain of “internal” problem. The code is designed for parallel computer, so that each element is “solved” on a separate processor. On each iteration step adjacent elements exchange “boundary conditions” (the values along vertical dashed lines, Figure 3). All elements are interconnected by the channels; 1D model of gas flow along the channels (“channel” problem) returns boundary conditions for each 2D element in the respective channel “window” (Figure 3). Internal and channel problems are coupled by local current density, so that the overall solution is obtained by iterations. A detailed description of the model is given in [10].

The results of the simulation are shown in Figure 4 (two elements at the inlet). Oxygen concentration in the catalyst layer is strongly nonuniform along  $y$ -axis. In front of the feed channel this concentration is higher, than in front of the ribs for current collection. The distribution of hydrogen on the anode side is similar. The rates of electrochemical reactions reproduce the patterns of feed gases concentration: they are higher in front of the respective channel.

The voltage current curve, obtained from this simulation (short-dashed line in Figure 2) deviates from the experiment. The reason is that our simple analytical theory, which gave coefficients for Q3D simulation, ignores nonuniformity of oxygen along  $y$ -axis.

Theoretical (long-dashed) curve in Figure 2 corresponds to a cell with the uniform oxygen concentration along  $y$ -axis. Figure 4 clearly shows, that in fact this concentration is strongly nonuniform. 1D analytical model “reduces” oxygen diffusion coefficient to compensate for this nonuniformity. In other words, 1D model generates voltage current curve of equivalent cell with the uniform oxygen concentration along  $y$ -axis and lower  $D_b$ .

To verify this idea we have performed a series of simulations, varying  $D_b$ . With three times larger  $D_b$  ( $8 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$ ), the simulated curve (solid line in Figure 2) agrees well with the experiment and with the theory. The difference between the two simulated curves hence give an estimate of voltage loss caused by local 2D effects and can serve as a measure of a quality of the flow field. Note, that the kinetic parameters ( $\alpha$ ,  $\gamma$  and  $i_*$ ) are correctly predicted by 1D theory.

### 4 DISCUSSION

Fuel cell performance depends on many parameters. It is convenient to separate them into three groups. The

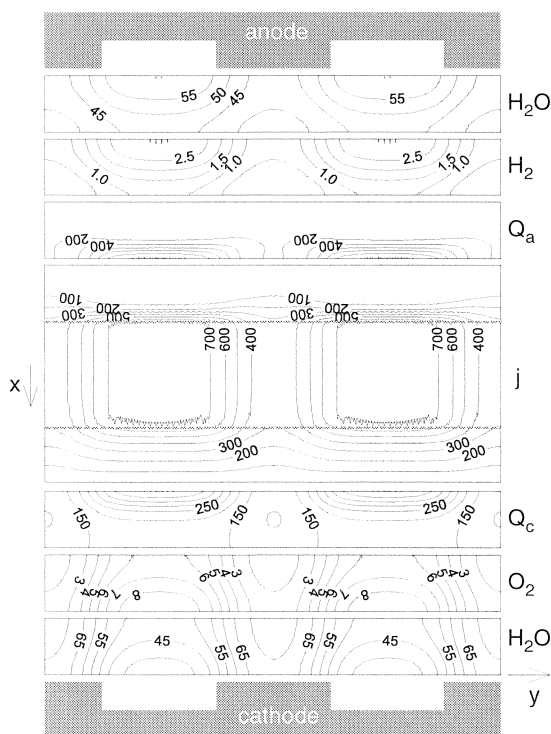


Figure 4: Molar concentrations of feed gases ( $\text{H}_2$  and  $\text{O}_2$ ), concentration of water vapor ( $\text{H}_2\text{O}$ ) and reaction rates ( $Q_a$ ,  $Q_c$ ) in the anode and the cathode catalyst layers.  $j$  is the proton current density in the catalyst layers and in the membrane ( $\text{mA cm}^{-2}$ ). All molar concentrations are in  $10^{-6}$  moles  $\text{cm}^{-3}$ , reaction rates are in  $\text{A cm}^{-3}$ . Grey dashed lines indicate the membrane/catalyst layers interfaces. Mean current density  $j_0$  is  $600 \text{ mA cm}^{-2}$ .

first group includes “local” parameters: oxygen diffusion coefficient, thickness of the membrane, catalyst and backing layers, and proton conductivity of the catalyst layer. The second group includes parameters of the flow field (geometry of channels and ribs). The third group constitute operational parameters (cell temperature, pressure and stoichiometry of feed gases).

The problem of optimal cell performance may be thought of as an optimization problem in a space of the order of 10 parameters. The parameters may interact nonlinearly with each other, so that experimentally determined positive trend in one parameter does not guarantee the direction towards global optimum. Clearly, attempts to find global optimum using trial-and-error method in a space of 10 parameters will prove disappointing.

Presented analytical theory deals with the parameters of the first and the third groups, ignoring along-the-channel and local 2D non-uniformities. If these effects are not large, the theory gives reasonable estimate

of basic properties of MEA and shows the influence of these properties on the overall cell performance. If the flow field is not optimal, the combination of theory and quasi-3D simulations enables to estimate the contribution of 2D and 3D effects. This combination thus makes it possible to characterize the MEA and the flow field.

## ACKNOWLEDGEMENTS

The author is grateful to Dr. F. Büchi (Paul Scherrer Institute, Switzerland) for the experimental data and useful discussions.

## REFERENCES

- [1] D. M. Bernardi and M. W. Verbrugge. *AIChE J.*, 37, 1151, 1991.
- [2] T. E. Springer, T. A. Zawodzinski, and S. Gottesfeld. *J. Electrochem. Soc.*, 138, 2334, 1991.
- [3] J. S. Yi and T. V. Nguyen. *J. Electrochem. Soc.*, 146, 38, 1999.
- [4] S. Um, C.-Y. Wang, and K. S. Chen. *J. Electrochem. Soc.*, 147, 4485, 2000.
- [5] S. Dutta, S. Shimpalee, and J. W. Van Zee. *J. Appl. Electrochem.*, 30, 135, 2000.
- [6] A. A. Kulikovskiy. *Electrochem. Comm.*, 4, 845, 2002.
- [7] A. A. Kulikovskiy. *Electrochem. Comm.*, 4, 318, 2002.
- [8] M. L. Perry, John Newman, and E. J. Cairns. *J. Electrochem. Soc.*, 145, 5, 1998.
- [9] M. Eikerling and A. A. Kornyshev. *J. Electroanal. Chem.*, 453, 89, 1998.
- [10] A. A. Kulikovskiy. *Num. Meth. Progr.*, 3, 150, 2002. <http://www.srcc.msu.su/num-meth/english/index.html> (free download).