

An empirical fuel cell polarization curve fitting equation for small current densities and no-load operation

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Abstract A logarithmic term is applied to account for the charge transfer overvoltage with most empirical polarization curve fitting equations for polymer electrolyte membrane fuel cells. The logarithmic term applied with state-of-the-art fitting equations is proportional to the logarithm of the cell output current density. This provides good fitting characteristics with large current densities, but results in significant deviations from measured current/voltage characteristics if small current densities or no-load operation are investigated. A modified logarithmic charge transfer overvoltage term utilising the exchange current density and an internal cell current density is therefore introduced to provide accurate fitting characteristics with small current densities and no-load operation. Fitting characteristics of this modified polarization curve fitting equation are investigated and compared to standard fitting equations.

Keywords Polymer electrolyte membrane fuel cell · Fuel cell model · Fitting equation · Polarization curve

Nomenclature

b Charge transfer overvoltage fitting parameter (V)
E Voltage (V)
E₀ Constant cell voltage fitting parameter (V)
E_{cell} Cell output voltage (V)
E_{OCV} Open circuit voltage (V)

E_{rev} Reversible cell voltage (V)
F Faraday constant (96,487 C mol⁻¹)
j Current density (A cm⁻²)
j₀ Exchange current density (A cm⁻²)
j₀ Charge transfer overvoltage fitting parameter (A cm⁻²)
j_{int} Internal current density (A cm⁻²)
j_{int} Charge transfer overvoltage fitting parameter (A cm⁻²)
j_i Mass transport overvoltage fitting parameter (A cm⁻²)
k Mass transport overvoltage fitting parameter (–)
m Mass transport overvoltage fitting parameter (V)
n_e Number of electrons (–)
n Mass transport overvoltage fitting parameter (cm² A⁻¹)
p Total pressure (Pa)
p_{O₂} Partial pressure of Oxygen (Pa)
R Gas constant (8.314 J mol⁻¹ K⁻¹)
R Ohmic overvoltage fitting parameter (Ω cm²)
S Mass transport overvoltage fitting parameter (–)
T Temperature (K)

Greek symbols

α Charge transfer coefficient (–)
α_S Mass transport overvoltage fitting parameter (V cm^{2k} A^{-1k})
α_P Mass transport overvoltage fitting parameter (V)
β Mass transport overvoltage fitting parameter (cm² A⁻¹)
μ Viscosity (kg m⁻¹ s⁻¹)

Subscripts

K Kim et al. [1]
L Lee et al. [4]
P Pisani et al. [3]
S Squadrito et al. [2]

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1 Introduction

Mathematical fuel cell models are applied in many different applications in design, control and optimization of fuel cells and fuel cell based power systems. Numerous fuel cell models have been developed since the late 1980s and early 1990s. Most of these models can either be categorized as mechanistic models (also known as ‘theoretical’ models) or as empirical models. Mechanistic fuel cell models are characterised by the fact that the fundamental mechanisms and processes governing fuel cell operation and performance are directly implemented into the model code. Thus, appropriate mathematical formulations describing e.g. the electrochemical reactions and the mass, species and charge transport phenomena have to be developed, and the required fuel cell materials and design parameters have to be determined for model calibration purposes.

Empirical fuel cell models, on the other hand, are primarily applied to reproduce experimentally-derived fuel cell performance data. Empirical models are therefore normally very limited in their performance prediction capability, but are nevertheless applied with many application-oriented analyses in scientific and industrial research and development because they are fast, robust and easy to calibrate. Empirical models are also a very interesting option if existing fuel cell stack hardware is to be modeled on a basis of simple stack performance measurements. Empirical fuel cell models normally do not require any material or design properties of the modeled fuel cell stack hardware, but are rather calibrated with a limited number of individual current/voltage measurements.

2 Model description

The purpose of an empirical polarization curve fitting equation is to represent a measured polarization curve—consisting of a number of individual current/voltage measurements—with a single analytical equation. By applying such a readily-calibrated analytical equation, the cell output voltage can thus be estimated for a specific current density and for the specific operating conditions applied in deriving the current/voltage measurements utilised for model calibration. A number of different empirical fuel cell polarization curve fitting equations can be found in the literature. Four polarization curve fitting equations are presented below. Fitting parameters are written with bold letters throughout this paper in order to provide a convenient visual distinction between fitting parameters and other model variables and constants.

The fitting equation of Kim et al. [1]:

$$E_{\text{cell}} = E_{0,K} - b_K \log(j) - R_K j - m_K \exp(n_K j) \quad (1)$$

The fitting equation of Squadrito et al. [2]:

$$E_{\text{cell}} = E_{0,S} - \frac{b_S}{\ln(10)} \ln(j) - R_S j + \alpha_S j^k \ln(1 - \beta j) \quad (2)$$

The fitting equation of Pisani et al. [3]:

$$E_{\text{cell}} = E_{0,P} - b_S \ln(j) - R_P j + \alpha_P \ln \left(1 + \frac{j}{j_l} S^{-\mu(1-j/j_l)} \right) \quad (3)$$

The fitting equation of Lee et al. [4]:

$$E_{\text{cell}} = E_{0,L} - b_L \log(j) - R_L j - m \exp(n_L j) - b_L \log \left(\frac{p}{p_{O_2}} \right) \quad (4)$$

All of these fitting equations consist of a constant cell voltage fitting parameter, a logarithmic term representing the charge transfer overvoltage, a linear term representing the ohmic overvoltage, and one (equations of Kim et al., Squadrito et al. and Pisani et al.) or two (equation of Lee et al.) additional terms describing the non-ohmic overvoltage due to mass and species transport limitations. The fitting equation of Kim et al.—used as a reference against which the modified fitting equation is being evaluated—e.g. applies a constant voltage fitting term $E_{0,K}$ (V), the magnitude of the charge transfer overvoltage is defined by the fitting parameter b_K (V), and R_K ($\Omega \text{ cm}^2$) is the ohmic resistance of the cell. It is important to mention that the constant voltage fitting term $E_{0,K}$ is normally neither equal to the open circuit voltage nor to the reversible thermodynamic cell voltage. Fitting parameters m_K (V) and n_K ($\text{cm}^2 \text{ A}^{-1}$) are not derived from physico-chemical considerations but only serve as curve-fitting parameters for the roughly exponential output voltage drop observed in high current density operation of low-temperature fuel cells.

If the natural logarithm is used instead of the common logarithm, the fitting parameter b has to be divided by 2.3. Natural and common logarithm are therefore equivalent with respect to their curve fitting characteristics. The common logarithm is used with the fitting equation development presented within this paper. Fitting Eqs. 1–4 are nevertheless presented with the natural or common logarithm-based terms used by the authors in their original work.

It is beyond the scope of this work to discuss the mass and species transport overvoltage term(s). These terms are primarily of interest with the medium and high current density region of a low-temperature fuel cell polarization curve. This is not of relevance with respect to the investigated low current density and no-load operation. The reader is referred to the original work for any further

information about these terms. This paper is rather focused on the first two terms of the empirical polarization curve fitting equations: the constant voltage term and the logarithmic charge transfer overvoltage term.

Neglecting the mass transport limitation term(s) and converting the natural logarithm-based terms in Eqs. 2, 3 into common logarithm-based terms, the cell output voltage can be computed as in Eq. 5. The neglect of mass transport limitation term(s) results in a simple fitting equation that is commonly used to represent the low current density region of a fuel cell polarization curve where only small mass transport limitations are present.

$$E_{\text{cell}} = E_0 - b \log(j) - Rj \quad (5)$$

In this, j is the current density and E_0 and b and R are fitting parameters. It is important to distinguish between E_{cell} (cell voltage if an external current is drawn from the cell), E_{OCV} (cell voltage if no external current is drawn from the cell) and E_0 . E_{cell} and E_{OCV} can be measured with an investigated cell during operation and are therefore strictly defined by the physico-chemical properties of a certain cell. E_0 , on the other hand, is a fitting parameter and can thus neither be measured nor directly related to any physico-chemical properties. The constant voltage fitting parameters E_0 (i.e. $E_{0,K}$, $E_{0,S}$, $E_{0,P}$, $E_{0,L}$) applied with the four reference Eqs. 1–4 will therefore normally not be identical to E_{cell} or E_{OCV} . Care therefore has to be taken to avoid confusion between mathematical fitting parameters and calculated physico-chemical properties.

Equation 5 fails to provide a reasonable cell output voltage prediction with small current densities and, in particular, with no-load operation. If the open circuit voltage E_{OCV} is to be computed, for instance, the cell output current density j is set to zero and the logarithmic term is therefore negatively infinite, whereas the predicted cell output voltage is positively infinite. In reality, the measured OCV will be somewhere around 950–1050 mV with most polymer electrolyte membrane fuel cells.

It is therefore not possible to fit the measured output voltage characteristics with small current densities as well as with no-load operation if a charge transfer overvoltage term is used where the logarithm of the cell output current density is computed.

One way of avoiding these incorrect output voltage predictions with small current densities would be to apply a linearization of the cell voltage with small current densities. A linear interpolation between the measured OCV and a fitted cell voltage computed with a certain minimum current density where the fitted polarization curve does not show a significant deviation from the measured values would be a feasible option, for instance. A linearization of the charge transfer overvoltage with small current densities

is also suggested in electrochemistry textbooks dealing with electron transfer reactions [5–7].

Introducing such a linearization into one of the above fitting equations is, however, not an elegant way of dealing with the problem. The purpose of having one analytical equation for cell voltage prediction is to have a simple and direct way of computing the current/voltage characteristics. The goal therefore is to develop one analytical equation that is valid over the whole range of current densities including no-load operation *as is*, so without any limitations, linearizations, or any other exceptions required to avoid the aforementioned problem.

This is possible by re-defining the logarithmic overvoltage fitting term. The charge transfer overvoltage for high cathodic currents, applying absolute values for current density and overvoltage, is defined as [5]:

$$|\eta| = \frac{2.3RT}{(1-\alpha)nF} \log\left(\frac{|j|}{j_0}\right) \quad (6)$$

All the constants and parameters located before the logarithm can be merged into fitting parameter b ; this is done with all four fitting Eqs. 1–4. The fundamental difference between Eq. 6 and the simplified fitting equations is found in the logarithmic term: all four fitting Eqs. 1–4 apply the logarithm of the current density, whereas the full analysis of electrode kinetics shows that the ratio of the current density and the exchange current density should be applied. The exchange current density is the current density present if no load is drawn from the cell and the anodic and cathodic currents with the electrode/membrane interfaces are thus in dynamic equilibrium. Modification one implemented with the modified logarithmic fitting term is thus to introduce the exchange current into the logarithmic fitting term.

A second aspect that has to be considered with the derivation of the logarithmic term is species crossover and internal currents. Internal currents (i.e. short-circuiting between anode and cathode due to the very small electronic conductivity of the polymer electrolyte membrane) basically ‘wastes’ electrons; the useable cell output current is therefore reduced by the internal cell current, as the electrons of the internal current do not pass through the external circuit.

Species crossover (i.e. primarily crossover of hydrogen from the anode to the cathode directly through the polymer electrolyte membrane) results in additional oxygen consumption, as oxygen is directly converted with hydrogen into water within the cathode active layer.

Due to the fact that the rate-determining process in (acidic) fuel cell operation is the charge transfer reaction at the cathode, any occupation of the cathode catalyst with reactions that do not generate a useable electric output

current inevitably leads to an increase in overvoltage required to generate a useable output current.

Due to the fact that the effects of internal currents and species crossover are essentially equivalent, both effects are considered with the combined internal equivalent current density j_{int} [8]. This is the second modification implemented with the logarithmic charge transfer overvoltage term: the equivalent internal cell current density is introduced into the logarithmic fitting term.

Considering exchange current density and internal cell current density as additional fitting parameters, Eq. 5 is thus modified to Eq. 7. The exchange current density j_0 and the internal cell current density j_{int} can also be determined using a least squares fitting procedure applied in determining the other fitting parameters of the empirical equation (i.e. \mathbf{b} and \mathbf{R} in Eq. 7).

$$E_{\text{cell}} = E_{\text{rev}} - \mathbf{b} \log \left(\frac{j + j_{\text{int}}}{j_0} \right) - \mathbf{R}j \quad (7)$$

E_{rev} is the reversible cell voltage and is computed as a function of the cell temperature and the partial pressures of active species according to the Nernst equation. This reversible cell voltage could be theoretically measured with an ‘ideal’ fuel cell if all the Gibbs free energy released by the reaction were available as electrical energy.

Introducing this reversible cell voltage into an empirical performance curve fitting equation provides a simple and well-defined way of computing the cell output voltage. This is done by subtracting the individual overvoltages from this reversible cell voltage. In fitting Eqs. 1–4 the overvoltage terms have to be subtracted from a constant voltage fitting term \mathbf{E}_0 that is not equal to a theoretical or actual cell voltage, but rather a purely mathematical fitting parameter.

According to Eq. 7 the cell is assumed to be operated ‘internally’ with a current density that is larger than the output current density present with the external electrical circuit. The case of the fuel cell being operated with zero current density, as would be the case if one of the standard fitting equations was applied in the computation of no-load cell operation, is thus eliminated. The cell output voltage can therefore also be computed accurately with very small current densities as well as with no-load cell operation.

Neglecting mass and species transport limitations, the OCV can be computed as:

$$E_{\text{OCV}} = E_{\text{rev}} - \mathbf{b} \log \left(\frac{j_{\text{int}}}{j_0} \right) \quad (8)$$

Introducing mass and species transport limitation term(s), this modified fitting equation can be applied to reproduce the fuel cell polarization curve characteristics over the whole range of current densities. The mass and species transport limitation term of the fitting equation of Kim

et al. is used in the example presented below. Any of the other mass and species transport limitation terms presented with fitting Eqs. 2–4 could equally well be applied. The advantage of introducing the modified logarithmic fitting approach is independent of the mass transport limitation term.

$$E_{\text{cell}} = E_{\text{rev}} - \mathbf{b} \log \left(\frac{j + j_{\text{int}}}{j_0} \right) - \mathbf{R}j - \mathbf{m} \exp(\mathbf{n}j) \quad (9)$$

Internal and exchange current density are additional fitting parameters and therefore have to be derived from a measured fuel cell polarization curve by applying a least squares fitting algorithm. Comparing this modified fitting equation with the standard fitting equation of Kim et al. two additional current density fitting parameters (\mathbf{j}_{int} and \mathbf{j}_0) are therefore introduced. The constant voltage fitting term \mathbf{E}_0 of the equation of Kim et al. is, on the other hand, not required.

Introducing the new logarithmic fitting term into one of the Eqs. 1–4 therefore requires only one additional fitting parameter.

3 Results and discussion

The comparison of measured and modelled cell performance is made with a polarization curve derived for a ‘CDL V2’ laboratory-scale single cell assembly. This single cell assembly has an active area of 25 cm² and is built from a commercially-available membrane electrode assembly as well as from commercially-available gas diffusion layers and carbon flow field plates. Design and measured characteristics of the ‘CDL V2’ single cell assembly are presented in [9, 10].

The polarization curve was obtained with the cell operated at 70 °C. Fuel was supplied with a stoichiometry of 1.5 and humidified at 60 °C; air was supplied with a stoichiometry of 2.2 and humidified at 50 °C. The cell resistance was determined to be 0.134 Ω cm² by applying electrochemical impedance spectroscopy with different current densities [9]. The area-specific cell resistance was therefore not determined with the fitting algorithm, but rather provided as a fixed model input parameter.

Figure 1 shows a comparison between the current/voltage measurements and the two fitted polarization curves. The solid line indicates the curve derived with the modified fitting equation (referred to as ‘Modified F.E.’) presented in Eq. 9; the dashed line indicates the curve derived with the standard fitting equation of Kim et al. (referred to as ‘Standard F.E.’) presented in Eq. 1. The fitting equation of Kim et al. was chosen as standard fitting equation because it is regularly applied as a basis for either developing and/or applying empirical fuel cell performance curves. The

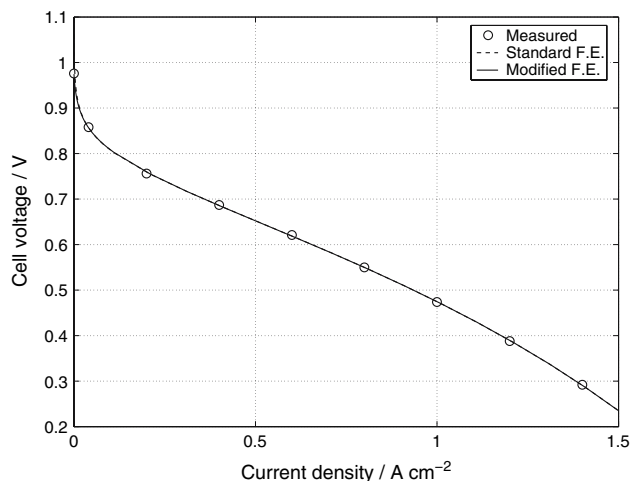


Fig. 1 Comparison of measured and fitted polarization curves

general characteristics and problems with respect to the investigated fitting behaviour at small current density and no-load operation are present with all four reference fitting Eqs. 1–4. Including all four reference fitting equations into the plots would thus only provide redundant information as all the fitting equations are capable of fitting performance curves with the medium and high current density regions very well, and all of them fail to do so at smaller current densities and no-load operation.

The standard and modified fitting equations provide excellent fitting characteristics with medium and high current densities; a slight difference between the two fitted curves is only obtained with very small current densities.

The low current density region of the fitted example polarization curve presented in Fig. 1. is shown in Fig. 2. A significant deviation between the two fitted curves is evident. The modified fitting equation provides an almost perfect fit with the OCV measurement as well as with the 40 mA cm^{-2} measurement. The standard fitting curve, however, fails to predict cell output voltages with current densities smaller than approximately 40 mA cm^{-2} . The difference between measured and fitted curve gradually increases when moving towards no-load cell operation. This difference is infinitely large under no-load conditions.

Fitting equations applying the standard logarithmic terms are therefore not able to predict cell output voltage with small current densities. The inability to predict the cell voltage with small current densities is completely independent of the actual polarization curve, as the standard logarithmic fitting always prevents a realistic cell voltage prediction with small current densities. This is not only true for the fitting equation of Kim et al. but also for the fitting equations of Squadrito et al. Pisani et al. and Lee et al. presented in Eqs. 2–4.

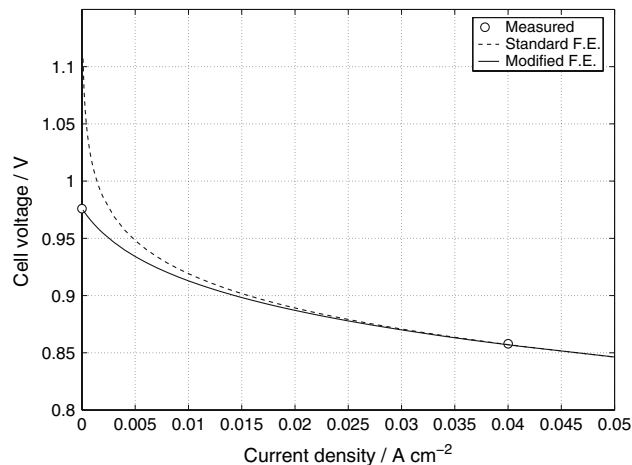


Fig. 2 Comparison of measured and fitted polarization curves; small current density region

The only case where a standard fitting equation would predict realistic cell output voltages with smaller current densities and no-load operation would be if the fitting parameter **b** is determined to be equal to zero, and the logarithmic term is therefore not utilised.

An overview of the fitting parameters determined by applying the standard fitting equation of Kim et al. (again referred to as ‘Standard F.E.’) and the fitting equation with the modified logarithmic term (again referred to as ‘Modified F.E.’) to the measured cell characteristics is shown in Table 1. A slight difference is derived between fitting parameters **b**, **m** and **n** derived with each of the two fitting equations. The constant voltage fitting parameter E_0 , derived with the standard fitting equation of Kim et al. deviates significantly from the measured open circuit voltage (E_0 of 0.784434 V versus OCV of 0.976 V). The standard fitting equation predicts an infinite OCV, whereas the modified fitting equation is able to predict the OCV almost perfectly.

The internal cell current density of 3 mA cm^{-2} compares well with the values of 4 mA cm^{-2} suggested as a reasonable value for a polymer electrolyte membrane fuel cell operation in [8]. The fitted exchange current densities are between the values reported for the exchange current densities reported for the anode (e.g. 0.6 A cm^{-2} applied in [11]) and the cathode electrode (e.g. $4.4 \times 10^{-7} \text{ A cm}^{-2}$ [11, 12]) of polymer electrolyte membrane fuel cells. An exact prediction of internal and exchange current densities cannot be expected with such a simple fitting algorithm, though. This could only be provided by limiting fitting parameter **b** to realistic values (fitting parameter **b** consists of different parameters and constants with pre-defined and limited ranges), and by using mass transfer limitation term(s) derived from fundamental physical and chemical

Table 1 Fitting parameters for the standard and the modified fitting equation

	E_0 (V)	b (V)	m (V)	n (cm ² A ⁻¹)	i_{int} (A cm ⁻²)	i_0 (A cm ⁻²)
Modified F.E. ^a	n/a	0.096212	0.047424	1.288587	3.0×10^{-3}	6.3×10^{-5}
Standard F.E. ^b	0.784434	0.093024	0.049369	1.270094	n/a	n/a

^a Fitting equation applying the modified logarithmic fitting term

^b Fitting equation of Kim et al. [1] applying the standard logarithmic fitting term

phenomena, rather than optimized curve fitting purposes, only.

4 Conclusions

A direct computation of the output voltage for small current densities and no-load operation is not possible with the analytical equations commonly applied in empirical modelling of polymer electrolyte membrane fuel cells. This is due to the fact that a charge transfer overvoltage term based on the logarithm of the cell output current density is applied with most empirical polarization curve fitting equations. Thus, the polarization curve can be predicted accurately for medium and high current densities, but the analytical equations fail to provide reasonable output voltage predictions for small current densities and no-load operation. This problem is eliminated by introducing a modified logarithmic charge transfer overvoltage fitting term. This modified fitting term applies a fitted exchange current density as well as a fitted internal cell current density. In addition, the constant voltage fitting term applied with most empirical polarization curve fitting equations can be eliminated, and the reversible cell voltage can be used instead. Only one additional fitting parameter is therefore required. Application of the modified fitting approach with example polarization curves showed excellent fitting characteristics; reasonable values are derived for the fitted exchange and internal current density. The fitting

equation therefore provides excellent polarisation curve fitting characteristics over the whole range of current densities; even very small current densities and no-load operation can be predicted accurately.

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References

1. Kim J, Lee S-M, Srinivasan S (1995) *J Electrochem Soc* 2670:2674
2. Squadrito G, Maggio G, Passalacqua E, Lufrano F, Patti A (1999) *J Appl Electrochem* 1449:1455
3. Pisani L, Murgia G, Valentini M, D’Aguanno B (2002) *J Power Sources* 192:203
4. Lee JH, Lalk TR, Appleby AJ (1998) *J Power Sources* 258:268
5. Hamann CH, Vielstich W (1998) *Elektrochemie*, 3rd edn. Wiley-VCH, Weinheim
6. Pletcher D (1991) *A first course in electrode processes*. The Electrochemical Consultancy, Romsey
7. Fisher AC (1996) *Electrode dynamics*. Oxford University Press, Oxford
8. Larminie J, Dicks A (2003) *Fuel cell systems explained*, 2nd edn. John Wiley & Sons, Chichester
9. Baumgartner WR (2007) *Characterization of PEM fuel cells*. Dissertation, Graz University of Technology
10. Baumgartner WR, Wallnöfer E, Schaffer T, Besenhard JO, Hacker V, Peinecke V, Prenninger P (2006) *Electrochem Soc Trans* 811:825
11. Berning T, Lu DM, Djilali N (2002) *J Power Sources* 284:294
12. Djilali N, Lu DM (2002) *J Therm Sci* 29:40