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# A simple and accurate method for high-temperature

## PEM fuel cell characterization

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## Abstract

A set of basic parameters for any polymer electrolyte membrane fuel cell (PEMFC) includes the Tafel slope  $b$  and the exchange current density  $j_*$  of the cathode catalyst, the oxygen diffusion coefficient  $D_b$  in the cathode gas–diffusion layer and the cell resistivity  $R_{cell}$ . Based on the analytical model of a PEMFC (A.A.Kulikovsky. *Electrochimica Acta* (2004) 617), we propose a two–step procedure allowing to evaluate these parameters for a high–temperature PEMFC. The procedure requires two polarization curves measured at different oxygen (air) stoichiometries. The method is validated using the experimental data obtained with the in–house designed cell. High quality of fitting confirms validity and accuracy of this approach. The physical background of the method is discussed.

## 1. Introduction

The heart of a high-temperature polymer electrolyte membrane fuel cell (HT-PEMFC) is a poly(benzimidazole) type polymer membrane doped with phosphoric acid [1]. This material has a good proton conductivity and it is stable in the temperature range 100 – 200 °C, which provides several advantages of HT-PEMFC over traditional low-T PEMFC. These advantages are: faster oxygen reduction reaction (ORR) kinetics, faster oxygen diffusivity and much better tolerance to impurities at elevated  $T$ . The latter property is especially valuable if the cell is fed with reformat hydrogen with relatively high concentration of CO.

Due to the absence of liquid water and related two-phase effects, modeling of HT-PEMFC is much simpler than modeling of conventional PEMFC. In recent years a number of numerical models for HT-PEMFC of various complexity and dimensionality have been developed [2,3,4]. These models utilize Butler-Volmer relation for ORR kinetics and they take into account diffusive/convective oxygen transport to the catalyst sites. In all these models, the membrane is assumed to be impermeable to gases and the cathode catalyst layer (CCL) is treated as an infinitely thin interface consuming protons and generating heat.

In spite of their great flexibility, numerical models are rather time-consuming, expensive and difficult to use. An attempt to take into account as many processes as possible usually leads to a model with the large number of constitutive parameters, many of which are poorly known.

There is a need for simpler models which include several (less than ten) basic parameters determining cell performance. [Such models are needed for e.g. fast control of the state of operating fuel cells and stacks by real time controllers.](#)

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A simple analytical model of a conventional PEM fuel cell [5] operates with just four parameters. These parameters are the Tafel slope  $b$  (or related transfer coefficient  $\alpha$ ), the superficial exchange current density  $j_*$  (or related volumetric exchange current density  $i_*$ ), the oxygen diffusion coefficient  $D_b$  in the cathode gas–diffusion layer (GDL) and the cell resistivity  $R_{cell}$ .

In this work, we use this model to process the experimental polarization curves of the high–temperature PEMFC. Based on the structure of model equations, a novel method is developed which gives the four parameters discussed above in two steps. On the first step *the difference* of two polarization curves measured for different oxygen stoichiometries is fitted giving  $b$  and  $D_b$ . On the next step one of the polarization curves is fitted to obtain the other two parameters,  $j_*$  and  $R_{cell}$ . Finally, the second polarization curve is used to verify the results.

High quality of curve fitting suggests that (i) the model is valid to description of HT–PEMFC and (ii) the parameters resulting from fitting are accurate and reliable. The physics behind the model equations is discussed.

## 2. Model for cell polarization curve

The model [5] utilizes the following assumptions.

1. The ORR kinetics obey Tafel law.
2. The oxygen transport loss across the cathode catalyst layer is negligible.
3. Oxygen is transported through the GDL due to a concentration gradient.
4. The membrane is impermeable to gases.
5. The air flow in the cathode channel is a plug flow (ideally mixed flow with

constant velocity).

6. The cell is isothermal.

For the discussion of these assumptions see [5] and the literature cited therein.

The hydrogen diffusivity and the rate of oxidation are very fast [6]; thus, the voltage loss on the anode side of HT-PEMFC can be safely ignored. Cell voltage  $V_{cell}$  is then

$$V_{cell} = V_{oc} - \eta - R_{cell}J \quad (1)$$

where  $V_{oc}$  is the cell open-circuit voltage (OCV),  $\eta$  is the voltage loss on the cathode side (polarization voltage) and  $R_{cell}$  represents all the resistive losses including the loss in the membrane.

A quasi-2D model of a non-flooded low-temperature PEMFC [5] gives the following expression for  $\eta$ :

$$\frac{\eta}{b} = \ln\left(\frac{c_{ref} f_{\lambda} J}{j_* c_h^0}\right) - \ln\left(1 - \frac{f_{\lambda} J}{j_{lim}}\right) \quad (2)$$

where

$$b = \frac{RT}{\alpha F} \quad (3)$$

is the Tafel slope,  $c_{ref}$  and  $c_h^0$  are the reference and inlet oxygen molar concentrations, respectively,  $j_*$  is the superficial exchange current density ( $A\ cm^{-2}$ ) of the cathode catalyst,  $J$  is the mean current density,

$$j_{lim} = \frac{4FD_b c_h^0}{l_b} \quad (4)$$

is the limiting current density due to oxygen transport through the GDL,  $D_b$  is the oxygen diffusion coefficient in the GDL of the thickness  $l_b$ , and

$$f_{\lambda} = -\lambda \ln \left( 1 - \frac{1}{\lambda} \right) \quad (5)$$

describes the effect of the oxygen stoichiometry  $\lambda$  on the voltage loss.

The first term on the right side of Eq.(2) is the voltage required to activate the ORR. The second term is the voltage loss due to the oxygen transport through the cathode GDL. It should be emphasized that Eq.(2) is not an empirical relation, it follows from solution of a system of conservation equations. In particular, Eq.(2) implies that the ORR kinetics obey the Tafel law

$$j = j_* \left( \frac{c_t}{c_{ref}} \right) \exp \left( \frac{\eta}{b} \right) \quad (6)$$

Here  $j$  is the local current density and  $c_t$  is the local oxygen concentration in the CCL.

Note that the Tafel slope in Eq.(2) coincides with the true kinetic value  $b$  appearing in the Tafel equation (6) only in the case of ideal transport of oxygen and protons across the CCL, as assumed in this work. In this case, the rate of ORR is distributed uniformly over the CCL thickness (see also discussion below).

Using Eq.(2) in (1) we get

$$V_{cell} = V_{oc} - b \ln \left( \frac{c_{ref} f_{\lambda} J}{c_h^0 j_*} \right) + b \ln \left( 1 - \frac{f_{\lambda} J}{j_{lim}} \right) - R_{cell} J \quad (7)$$

Eq.(7) contains 4 fitting parameters:  $b$ ,  $j_*$ ,  $j_{lim}$ , and  $R_{cell}$  (we assume  $c_{ref} = c_h^0$ ).

Direct fitting of polarization curves in a space of four parameters is rather difficult and computationally expensive task [7]. The largest problem of fitting in a space of many parameters is that none of the fitting algorithms guarantees convergency to the global minimum of the merit function and a “good” local minimum is found instead. The number of minima of a merit function dramatically increases with the problem dimensionality in a parameter space, and hence reduction of this dimensionality is

very desirable. Much better alternative to a direct 4-parametric fitting provides the following idea.

Writing Eq.(7) for the two oxygen stoichiometries  $\lambda_1$  and  $\lambda_2$  and subtracting the resulting equations we get

$$V_{cell}(\lambda_1) - V_{cell}(\lambda_2) = -b \ln \left( \frac{f_{\lambda_1}}{f_{\lambda_2}} \right) + b \ln \left( \frac{j_{lim} - f_{\lambda_1} J}{j_{lim} - f_{\lambda_2} J} \right) \quad (8)$$

We see that  $R_{cell}$ ,  $j_*$  and  $V_{oc}$  are excluded and Eq.(8) contains only two fitting parameters:  $b$  and  $j_{lim}$ . Therefore, measuring two polarization curves for different  $\lambda$  and subtracting one curve from another, we get a new curve which can easily be fitted by Eq.(8) in a space of just two parameters.

The second step is to use  $b$  and  $j_{lim}$  to fit one of the “source” polarization curves. This step gives another two parameters  $j_*$  and  $R_{cell}$ . The second polarization curve is then used to verify the results of fitting. To validate this method we measured two polarization curves at different  $\lambda$ ; the details of measurements are given in the next section.

### 3. Experimental

The membrane electrode assemblies have been prepared using in-house developed gas diffusion electrodes and poly(2,5-benzimidazole) (ABPBI or ab-PBI) supplied by FuMA-Tech GmbH as membrane polymer. ABPBI is chemically closely related to PBI (AB reflects the fact that the polymer is formed in head-tail variety, Figure 1). This material has several advantages over the conventional PBI polymer. ABPBI is easy to synthesize with very high molecular weights; as a result it absorbs more phosphoric acid than PBI and yields the membranes with high proton conductivity [8]. Compared to PBI, ABPBI has less frequently been used as

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3 membrane material in HT-PEMFC cells [9,10,11,12].  
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6 While the raw ABPBI membrane is 30 micrometers thick, the thickness of  
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8 ABPBI soaked with phosphoric acid amounts to  $70 \mu\text{m}$ . Gas diffusion electrodes  
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10 (GDEs) with a platinum loading of  $1.2 \text{ mg cm}^{-2}$  have been prepared by coating an ink  
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12 containing 20 wt.% Pt/C catalyst (HiSPEC 3.000, Johnson Matthey) and PTFE  
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14 (Dyneon) onto a woven GDL (HT 1400-W, BASF Fuel Cell Inc.) via an automated  
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16 doctor blade technique followed by a drying step.  
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20 GDEs have been previously impregnated with about  $20 \text{ mg cm}^{-2}$  of  
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22 phosphoric acid. MEAs with the active area  $14.4 \text{ cm}^2$  have been assembled by  
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24 contacting two such GDEs with an undoped ABPBI membrane without a preceding  
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26 hot-pressing step (cf. [13]). Acid uptake of the membrane is assumed to happen when  
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28 the MEA is heated up to the operating temperature of the fuel cell. The CCL thickness  
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30 was estimated to be  $150 \mu\text{m}$ .  
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35 The polarization curves were measured with the MEA fixed between graphite  
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37 bipolar plates with triple serpentine flow fields at a cell temperature of  $160 \text{ }^\circ\text{C}$  and  
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39 ambient pressure pure hydrogen and chemically dried air as the reactants.  
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43 During the recording of the polarization curves the stoichiometric excesses of  
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45 the gases were adjusted to  $\lambda_{\text{Anode/Cathode}} = 2.0/2.0$  or  $3.0/3.0$  for current densities greater  
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47 than  $0.025 \text{ A cm}^{-2}$ . Below  $0.025 \text{ A cm}^{-2}$  the gas flows have been fixed  
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49 corresponding to  $\lambda = 2/2$  and  $3/3$ , respectively, at  $j = 0.025 \text{ A cm}^{-2}$ . For each data  
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51 point, after a hold time of at least 30 seconds the cell voltage has been measured and  
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53 averaged during 30 seconds.  
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## 4. Results and discussion

### 4.1. Parameters resulted from fitting

Figure 2a shows the polarization curves measured for  $\lambda = 2$  and 3. Figure 2b depicts the difference of these curves (solid line) and Eq.(8) (dashed line) fitted to the data. As can be seen, in a large range of current densities (from 0.025 to 0.92 A cm<sup>-2</sup>) the quality of fitting is very good. The deviation of theory and experiment at larger currents (above 0.92 A cm<sup>-2</sup>) will be discussed below. The parameters  $b$  and  $j_{\text{lim}}$  resulted from fitting are listed in Table 1. Note that the model curve in Figure 2b is very sensitive to the value of  $b$ : a 10% variation in  $b$  significantly worsens the quality of fitting.

Next step is to fit one of the polarization curves using (7). With  $b$  and  $j_{\text{lim}}$  obtained from the first step, Eq.(7) contains only two fitting parameters:  $j_*$  and  $R_{\text{cell}}$  (we assume  $c_{\text{ref}} = c_h^0$ ). The open-circuit voltage was estimated to be 1.13 V [2].

The results of fitting are displayed in Figure 3. The parameters  $j_*$  and  $R_{\text{cell}}$  were determined from fitting of the curve for  $\lambda = 2$ ; the other curve ( $\lambda = 3$ ) was then plotted with the obtained set of parameters and  $\lambda = 3$ . Figure 3 shows several interesting things.

For both curves in this Figure the quality of fitting up to  $J = 0.6$  A cm<sup>-2</sup> is excellent: in this region the experimental and model curves are practically indistinguishable. This suggests that the model [5] works well for HT-PEMFC. Due to the absence of liquid water in HT-PEMFC, it seems to work much better for these cells than for a conventional low-temperature PEMFC.

In a low-T PEMFC, a lack of liquid water at the oxygen channel inlet leads to

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3 membrane drying which increases the local membrane resistivity. Close to the  
4 channel outlet the excess of water may flood the GDL thereby hindering oxygen  
5 transport to the catalyst sites. Both these effects lead to *local* non-uniformities in the  
6 membrane resistivity and in the oxygen diffusivity, which are not accounted for by a  
7 simple model [5]. Thus, for low-T PEMFC the model above is applicable in a rather  
8 narrow range of operating conditions, when the membrane is fully humidified and no  
9 flooding occurs [14]<sup>1</sup>.

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20 In HT-PEMFC, liquid water may exist only in very small pores and we may  
21 expect that the effect of these pores on cell performance is marginal. This makes the  
22 limits of validity of the model above much wider.

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27 The parameters resulted from the fitting (Table 1) seem to be quite reasonable,  
28 except lower than expected oxygen diffusion coefficient  $D_b$  in the GDL ( $D_b$  is  
29 roughly ten times smaller than the oxygen diffusivity in atmospheric pressure air at  
30 160 °C  $D_{air} = 0.406 \text{ cm}^2 \text{ s}^{-1}$  [16]). Low value of  $D_b$  suggests problems with  
31 oxygen transport due to the uncontrollable amount of liquid phosphoric acid in the  
32 GDL [12].

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42 The experimental curves *are not* fitted well by model equations above  
43  $J = 0.92$  in Figure 2b and above  $J = 0.6$  in Figure 3. This suggests that in the high-  
44 current region, the distribution of reaction rate across the cathode catalyst layer is  
45 non-uniform. Two reasons may lead to this non-uniformity: poor oxygen or poor  
46 proton transport through the catalyst layer. In the first case the peak of the ORR rate is  
47 located close to the GDL/CCL interface, where the oxygen concentration is maximal.  
48 In the second case this peak is located at the membrane/CCL interface, where protons  
49 are “cheaper” [6].

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<sup>1</sup> Incorporation of water effects lead to a more complicated model which can be solved analytically

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3 In both cases the non-uniformity of ORR distribution across the CCL  
4 manifests itself as the *doubling of apparent Tafel slope* [6,17] and this seems to be the  
5 most probable explanation of the deviations of theory and experiment in Figures 2  
6 and 3. In Figure 3 the experimental curves decay faster, than the model curves; this  
7 fact works in favor of the conjecture above. Unfortunately, polarization curves  
8 provide only integral characteristic of a fuel cell, which is not sufficient to distinguish  
9 between the two mechanisms of the Tafel slope doubling.  
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20 Though the Tafel slope doubling is not described by our simple model, the  
21 method proposed allows us to determine the “critical” current density  $J_{crit}$ , above  
22 which doubling affects the polarization curve. Starting from  $J = J_{crit}$ , fitting Eq.(8) to  
23 the difference of the experimental polarization curves fails. From Figure 2b it can be  
24 seen that  $J_{crit} \approx 0.9 \text{ A cm}^{-2}$ .  
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33 Note that the Tafel slope doubling can be accounted for [18]. However, this  
34 gives additional parameter in model equations, which makes fitting less reliable.  
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37 The four parameters discussed in this work can, in principle, be determined  
38 separately in specially designed experiments. However, delicate experimental  
39 methods are time-consuming and they require cell disassembling. In contrast, the  
40 method discussed enables fast *in situ* measuring of cell parameters, which is important  
41 for many real-time applications.  
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#### 50 4.2. Transport loss in the catalyst layer

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53 The model above is valid provided that the oxygen transport loss in the CCL  $\eta_{CCL}^{conc}$  is  
54 much smaller than this loss in the GDL  $\eta_{GDL}^{conc}$  (the second term in Eq.(2)). Recently it  
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only in the limiting case of large overpotential [15].

has been shown that  $\eta_{CCL}^{conc}$  is negligible if the oxygen diffusion coefficient in the CCL

$D_t$  exceeds the characteristic value  $D_*$  given by [19]

$$D_* = \frac{l_t J}{4Fc_t^0} \quad (9)$$

where  $l_t$  is the CCL thickness and  $c_t^0$  is the oxygen molar concentration at the CCL/GDL interface. The latter value is related to the oxygen concentration in the channel [18]

$$c_t^0 = c_h^0 \left( 1 - \frac{J}{j_{lim}} \right) \quad (10)$$

Here for the estimate we take all values in Eqs.(9) and (10) at the channel inlet.

Substituting (10) into Eq.(9) we arrive at

$$D_* = \frac{l_t J}{4Fc_h^0 \left( 1 - \frac{J}{j_{lim}} \right)} \quad (11)$$

The dependence  $D_*(J)$  plotted with the data from Table 1 is shown in Figure 4. The green (shaded) area in this Figure indicates the region where  $D_* \leq D_b$ .

This Figure suggests that in our cell the oxygen diffusivity in the CCL is nearly the same as in the GDL, i.e.,

$$D_t \approx D_b \quad (12)$$

Indeed, if Eq.(12) holds, then  $\eta_{CCL}^{conc}$  is small up to  $J \approx 1 \text{ A cm}^{-2}$  (Figure 4); this value agrees well with  $J_{crit} = 0.9 \text{ A cm}^{-2}$  obtained from Figure 2b. Furthermore, if  $\eta_{CCL}^{conc}$  were large, fitting of the curve Eq.(8) to the data in Figure 2b would hardly be possible, since Eq.(8) ignores the Tafel slope doubling.

With  $D_t \approx D_b$ , the major transport loss occurs in the GDL, since the GDL thickness is roughly 3 times larger than the CCL thickness. In other words, in our

experiments transport loss in the CCL can be neglected.

#### 4.3. Can $\alpha$ be determined from the activation region?

An alternative and widely used method of  $\alpha$  determination is fitting the cell polarization curve in the region of small current densities (activation region). However, this method gives reliable results only when the cell resistivity is known.

To illustrate the pitfall due to the resistive term we note that in the activation region the transport term is negligible and Eq.(7) simplifies to

$$V_{cell} = V_{oc} - b \ln \left( \frac{J}{J_*} \right) - RJ \quad (13)$$

where  $J_* = c_h^0 j_* / (c_{ref} f_\lambda)$ .

If  $R = 0$ , from Eq.(13) it follows that the Tafel slope is given by the derivative

$$b = - \frac{\partial V_{cell}}{\partial (\ln J)} \quad (14)$$

If  $R \neq 0$ , using the identity  $RJ = R \exp(\ln J)$  and calculating this derivative with Eq.(13), we obtain

$$- \frac{\partial V_{cell}}{\partial (\ln J)} = b + RJ \quad (15)$$

We see that the resistive term  $RJ$  introduces error in  $b$ , and the larger the current, the larger this error. A 10%–error in  $b$  due to this term is reached at the current density

$$J_{10} = \frac{0.1b}{R}$$

Taking for the estimate the data obtained from fitting (Table 1) we get

$$J_{10} \approx 0.02 \text{ A cm}^{-2}.$$

Therefore, if  $R$  is unknown, then to derive  $\alpha$  with 10% accuracy the polarization curve should be fitted in the region of currents below  $0.02 \text{ A cm}^{-2}$ .

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3 However, in this region the cell works close to the equilibrium where the applicability  
4 of Tafel equation can be violated. The use of the full Butler–Volmer equation also is  
5 problematic, since this equation contains more unknown parameters (the transfer  
6 coefficient of the reverse reaction and the water reference concentration).  
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12 Therefore, the method proposed in this work gives a more reliable and  
13 accurate  $\alpha$  in the situations when  $R$  is unknown. This method gives  $\alpha$  on the first  
14 step of fitting, when the resistive term does not affect the data (the difference of two  
15 polarization curves does not contain  $RJ$ ). This property of the method is especially  
16 useful if  $R$  changes with the current density.  
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## 25 26 5. Conclusions

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28 We report a novel method for *in-situ* determination of the basic kinetic and transport  
29 parameters of a high-temperature PEMFC. The method is based on the model for  
30 polarization curve of a PEMFC [5], which takes into account the effect of oxygen  
31 stoichiometry on cell performance.  
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38 The method requires measuring two polarization curves for different oxygen  
39 stoichiometries. The difference of two curves contains neither the resistive term, nor  
40 the exchange current density. Fitting this difference with the equation which follows  
41 from the model [5] yields the Tafel slope  $b$  and the oxygen diffusion coefficient in  
42 the GDL  $D_b$ .  
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50 These two parameters are then used in a direct fitting of the polarization  
51 curves. This step yields two missing parameters: the exchange current density  $j_*$  and  
52 the cell resistivity  $R_{cell}$ . The method is validated against the experimental data  
53 obtained with the in-house cell. The method is routinely used in our Institute to  
54 characterize the cells.  
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3 The proposed method is limited to the situation when the transport loss of  
4 oxygen in the cathode catalyst layer is small. If the nature of current limitation in the  
5 cell is unknown, the region of the polarization curve close to the limiting current  
6 density should be excluded from the fitting. The method is particularly useful when  
7 the cell resistance is unknown or if it changes with the cell current, so that the  
8 common practice using IR—free voltage to extract the ORR kinetics is impossible.  
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## Figure captions

1. Repeating units of PBI (= poly(2,2-(m-phenylene)-5,5-benzimidazole), left) and ABPBI (=poly(2,5-benzimidazole), right).
2. (Color online) (a) Experimental polarization curves. (b) Their difference (solid line) and fitting curve (8) (dashed line). Fitting parameters are listed in Table 1. Cell temperature 160 °C, pure hydrogen on the anode side and dried air at the cathode side; both sides are at atmospheric pressure.
3. (Color online) Experimental polarization curves (solid) and fitted model (dashed lines). for oxygen stoichiometry 2 (a) and 3 (b). Fitting parameters are listed in Table 1.
4. (Color online) The characteristic oxygen diffusion coefficient in the catalyst layer  $D_*$  (Eq.(11)) vs. the cell current density  $J$  (solid blue line). Dashed line – the oxygen diffusion coefficient in the GDL  $D_b$  obtained from fitting. The green (shaded) domain indicates the “allowed” region for the oxygen diffusivity  $D_t$  in the catalyst layer. In this region, the transport voltage loss in the CCL is small.

$b, V$	$\alpha$	$j_{\text{lim}},$ A cm <sup>-2</sup>	$D_b,$ cm <sup>2</sup> s <sup>-1</sup>	$j_*, A \text{ cm}^{-2}$	$i_*, A \text{ cm}^{-3}$	$R_{\text{cell}}, \Omega \text{ cm}^2$
0.048	0.777	1.34	$2.38 \times 10^{-2}$	$1.5 \times 10^{-5}$	$10^{-3}$	0.26

**Table 1. Results of curve fitting (Figures 2, 3). Volumetric exchange current density  $i_* = j_*/l_t$ ,**

**where  $l_t = 1.5 \times 10^{-2}$  cm is the catalyst layer thickness. Cell temperature is 160 °C, OCV is 1.13**

**V, GDL thickness  $l_b = 4 \times 10^{-2}$  cm.**

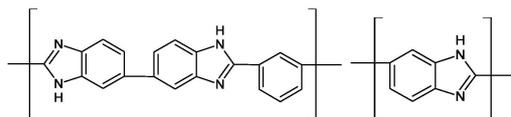


Figure 1. Repeating units of PBI (= poly(2,2-(m-phenylene)-5,5-benzimidazole), left) and ABPBI (=poly(2,5-benzimidazole), right).

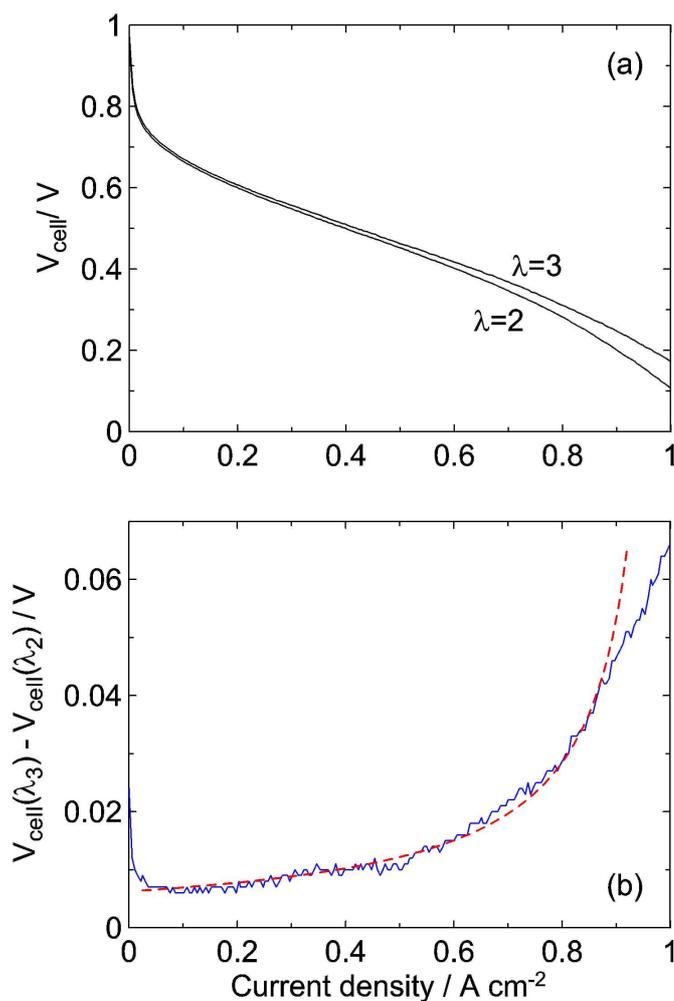


Figure 2. (Color online) (a) Experimental polarization curves. (b) Their difference (solid line) and fitting curve (8) (dashed line). Fitting parameters are listed in Table 1. Cell temperature 160 °C, pure hydrogen on the anode side and dried air at the cathode side; both sides are at atmospheric pressure.

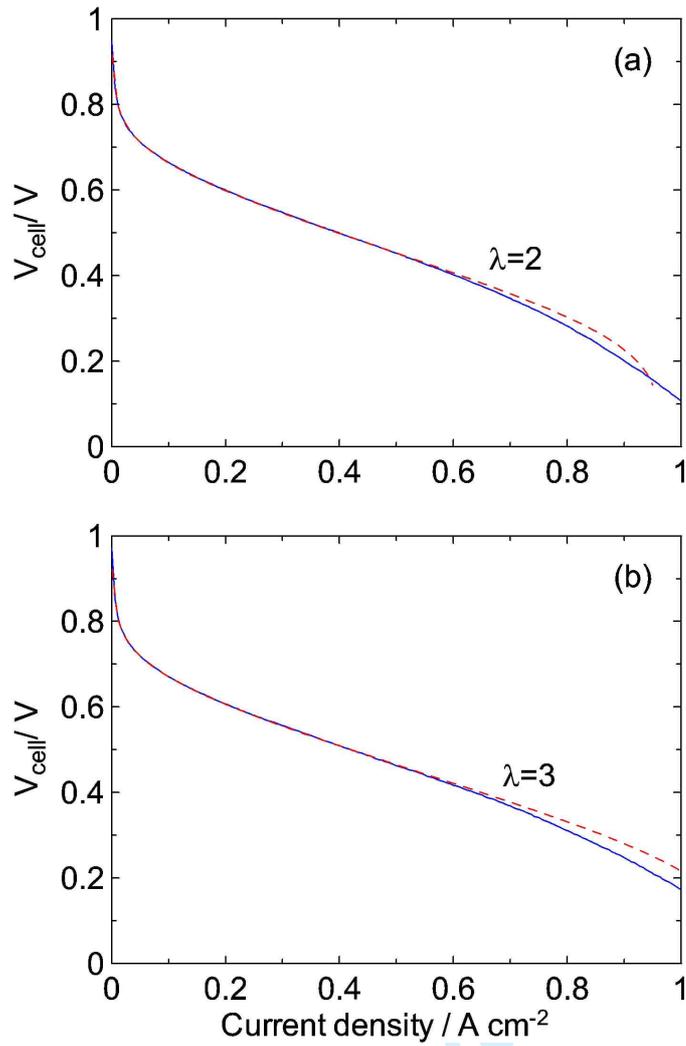


Figure 3. (Color online) Experimental polarization curves (solid) and fitted model (dashed lines), for oxygen stoichiometry 2 (a) and 3 (b). Fitting parameters are listed in Table 1.

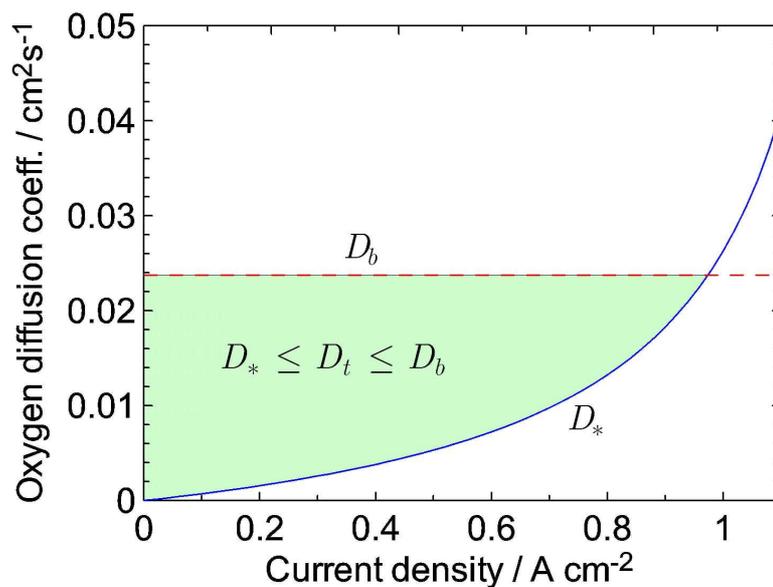
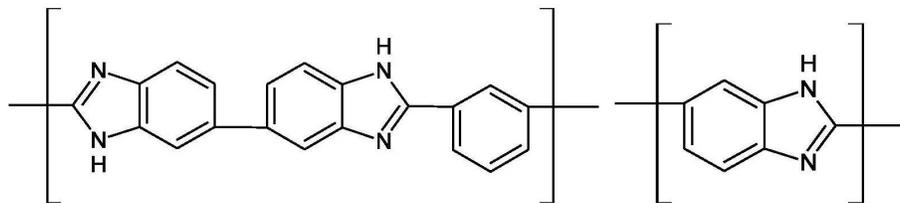
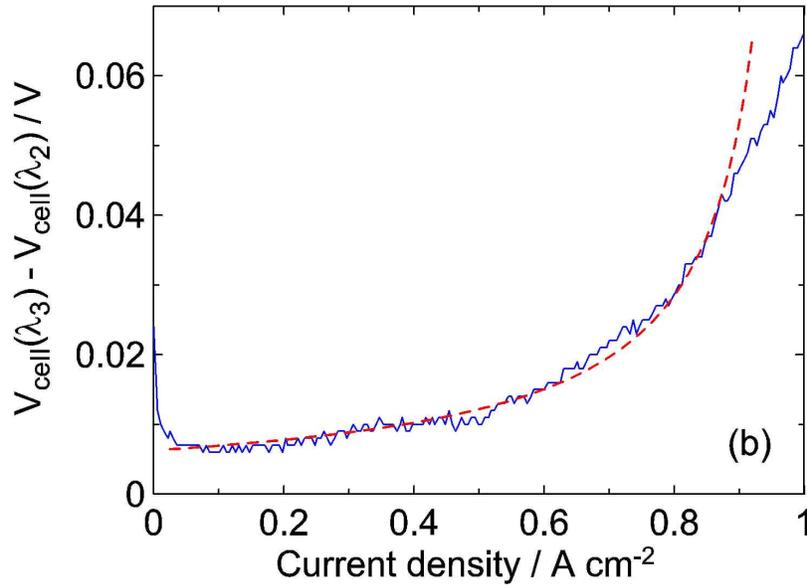
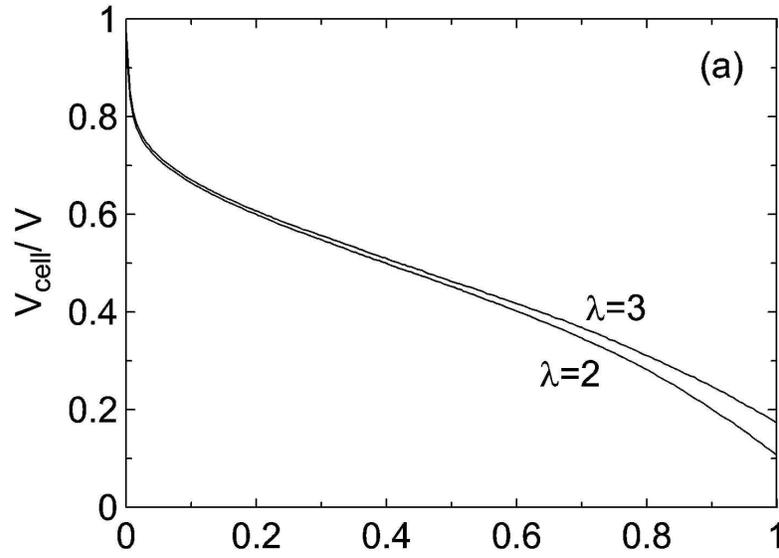


Figure 4. (Color online) The characteristic oxygen diffusion coefficient in the catalyst layer  $D_*$  (Eq.(11)) vs. the cell current density  $J$  (solid blue line). Dashed line – the oxygen diffusion coefficient in the GDL  $D_b$  obtained from fitting. The green (shaded) domain indicates the “allowed” region for the oxygen diffusivity  $D_t$  in the catalyst layer. In this region, the transport voltage loss in the CCL is small.

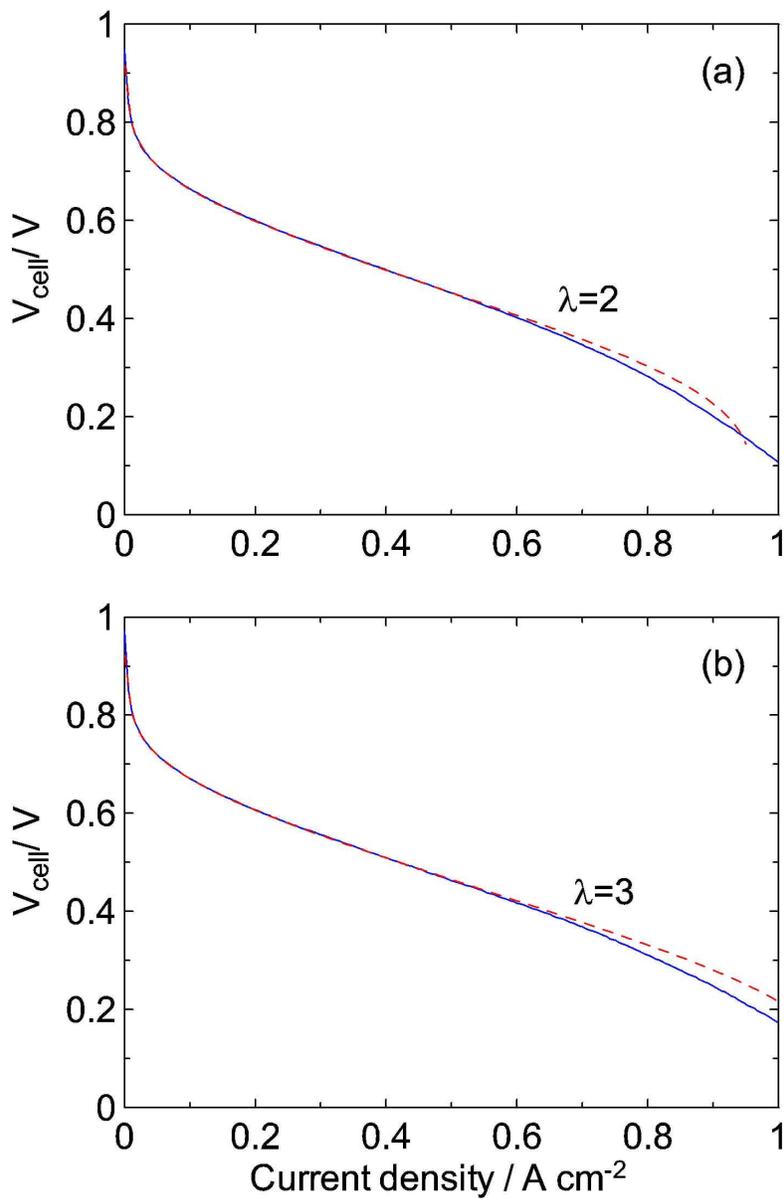


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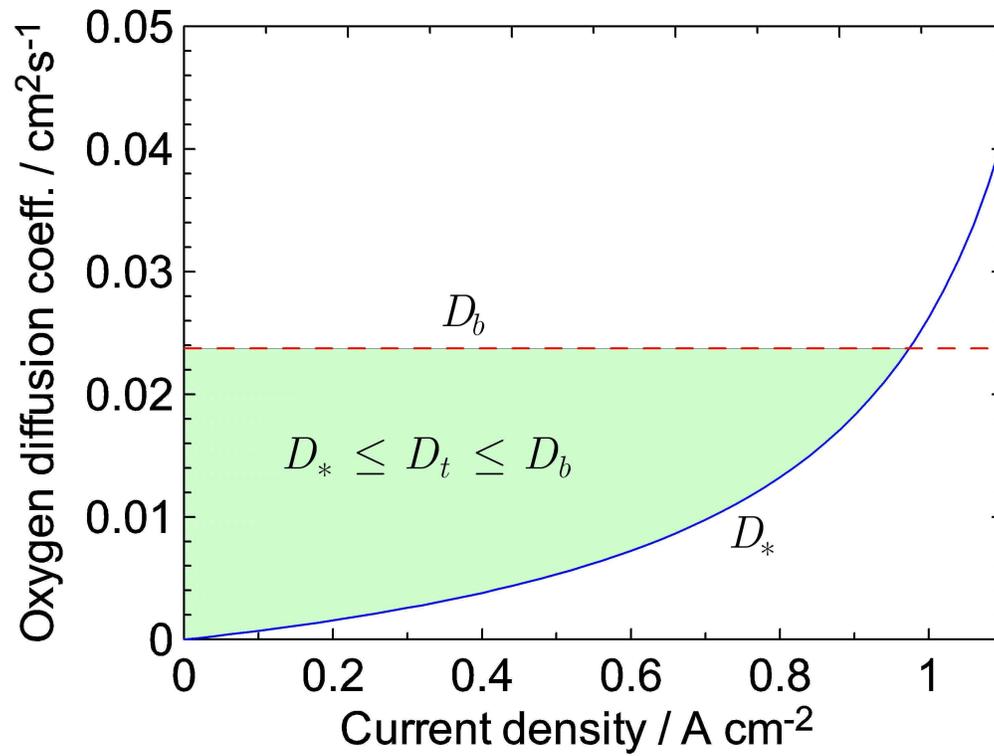


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