

Reference Electrode Positioning in PEM Fuel Cell at a Parabolic Anode Tip

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Abstract

Two-dimensional (2D) distribution of proton exchange membrane (PEM) fuel cell cathode overpotential η in the vicinity of parabolic anode tip is described by nonlinear Poisson–Boltzmann equation. The 2d shape of η is calculated numerically for the anode tip curvature varying by two orders of magnitude. It

is shown that the reference electrode for measuring cathode overpotential can be located at a distance on the order of two characteristic lengths from the anode tip. For typical PEM fuel cell parameters, this distance is about 5.5 cm. A compact design for the reference electrode positioning is suggested.

Keywords: Modeling, PEM Fuel Cell, Reference Electrode

1 Introduction

Oxygen reduction reaction (ORR) overpotential η is of large interest for PEM fuel cell design, testing and control. Measuring η is usually performed by means of reference electrode (RE) technique [1,2]. Reference electrodes of internal type require rather bulky salt bridge connection [3], which is suitable for research but hardly applicable for testing of commercial stacks. Below, we consider RE of external type.

Typically, the external RE is positioned over the membrane at a certain distance from the anode and cathode edges (see Figure 1 in Ref. [4]). However, this design requires precise alignment of the electrode edges. It has been shown that even a small misalignment leads to strong distortions of measured potential; the problem has been extensively studied in fuel cell literature [5–8]. Recently, it has been suggested to place RE at a certain distance from the straight anode edge over the large cathode [4]. This arrangement eliminates the problem of electrodes alignment; however, the distance between the anode edge and RE appears to be rather large (see below). Later, analytical shape of the ORR overpotential at a circular anode edge over the infinite cathode has been calculated [9]. The solution shows that the distance between the anode edge and RE can be significantly lowered if the anode is curved.

In this work, we consider PEM fuel cell with the parabolic anode tip located above the large cathode (Figure 1a). Suppose that the cell works under the load and let η be the positive by convention ORR overpotential. Let in the working cell domain, i.e., between the anode and cathode $\eta = \eta_0$. Qualitatively it is clear that η decreases from η_0 down to zero with the distance from the anode tip (Figure 1b). It is also evident, that

the rate of η decay with this distance is maximal at the symmetry axis x of the problem. It has been shown that the membrane potential Φ increases with the distance from the tip, reaching the value of η_0 as $\eta(x)$ approaches zero [9] (Figure 1b). Thus, by placing a hydrogen-fed reference electrode at the point where $\eta(x) \approx 0$, one can measure $\Phi \approx \eta_0$ (Figure 1b). Below, we calculate the 2D shapes of the ORR overpotential and membrane potential around the parabolic anode tip. We show that at the symmetry axis, the point where membrane potential reaches the value of η_0 is located at the distance of about two Debye lengths of the problem. In the dimension units, for typical PEM fuel cell this distance is about 5.5 cm.

2 Model


In the anode-less area, the cathode overpotential is described by the Poisson–Boltzmann (PB) equation, which in dimensionless form reads [4, 9]

$$\Delta \tilde{\eta} = \sinh(\tilde{\eta}) \quad (1)$$

where $\Delta \tilde{\eta} \equiv \tilde{\eta}_{xx} + \tilde{\eta}_{yy}$ is the 2d Laplacian in Cartesian coordinates. Here, the dimensionless variables are scaled according to

$$\tilde{x} = \frac{x}{\lambda_D}, \quad \tilde{y} = \frac{y}{\lambda_D}, \quad \tilde{\eta} = \frac{\eta}{b} \quad (2)$$

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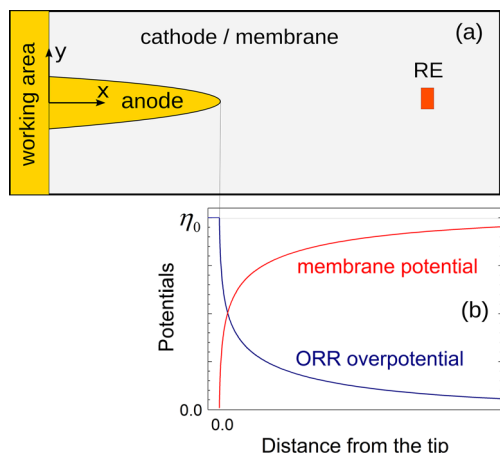


Fig. 1 (a) Schematic of the fuel cell with the planar tip anode over large cathode. RE indicates position of the reference electrode. (b) The shape of ORR overpotential η and of the membrane potential Φ with the distance from the tip along the x axis. η_0 is the overpotential in the working domain.

where

$$\lambda_D = \sqrt{\frac{\sigma_m b l_m}{j_{ox}}} \quad (3)$$

is the characteristic length of η variation in the problem (Debye length, see below). Here, σ_m is the proton conductivity of bulk membrane, b is the ORR Tafel slope, l_m is the membrane thickness, $j_{ox} = l_t i^*$ is the superficial ORR exchange current density (A cm^{-2}), l_t is the CCL thickness, and i^* is the volumetric ORR exchange current density (A cm^{-3}).

Analytical solution of one-dimensional version of Eq. (1) has been derived in classic works of Gouy and Chapman, who considered the problem of potential distribution at the surface of metal electrode immersed in a currentless electrolyte [10, 11]. Quite interestingly, the shape of ORR overpotential in the system depicted in Figure 1 is also described by the PB equation. In the theory of Gouy and Chapman, the right side of Eq. (1) represents the difference of Boltzmann distributions of positive and negative ions (the space charge) in the electric field, while here, the right side approximates the ORR rate minus the rate of the reverse reaction of water electrolysis. The analogy with Gouy–Chapman model justifies introduction of λ_D as the Debye length of the problem. For details of Eq. (1) derivation see [4, 9].

Eq. (1) describes also the electric field in gaseous plasma near a macroscopic charged particle [12]. Dyachkov [12] reported analytical solution to Eq. (1) for the spherical and axial symmetries in the form of infinite series. Zholkovskij et al. [13] derived matched asymptotic solution for the PB equation with spherical symmetry. In [8], similar technique has been used to derive approximate analytical solution to the PB equation with planar radial symmetry. The latter problem describes ORR overpotential distribution around a circular anode in a PEM fuel cell with infinitely large cathode.

In this work, numerical solution of Eq. (1) is obtained for the parabolic anode over the large cathode (Figure 1). From practical point of view, the parabolic anode is of large interest, as the anode tip curvature can easily be regulated. The solution indicates optimal distance from the anode tip for positioning of a reference electrode.

3 Numerical Solution

A feature of Eq. (1) in the geometry of Figure 1 is a huge gradient of overpotential at the anode edge. Care should be taken to avoid numerical instabilities, due to this gradient. Eq. (1) has been converted to the finite-difference form, using a standard approximation of Laplacian on a 5-point computational molecule. Inside the body of the anode tip and in the nearest vicinity of the anode edge, the computational mesh along the y -coordinate was uniform, while the mesh along the x -coordinate has been constructed in order to locate the nodes exactly at the anode edge. This allows us to minimize numerical perturbations at the edge. The rest of the computational domain was covered by exponentially expanding along the x - and y -axes mesh, as in this domain, the variation of overpotential is small.

Eq. (1) was solved, using a well-known symmetric successive overrelaxation (SSOR) Poisson solver [14]. The nonlinear term on the right side of Eq. (1) has been linearized between two successive iterations according to

$$\sinh(\tilde{\eta}_{i,j}^{n+1}) = \sinh(\tilde{\eta}_{i,j}^n) + \cosh(\tilde{\eta}_{i,j}^n) (\tilde{\eta}_{i,j}^{n+1} - \tilde{\eta}_{i,j}^n) \quad (4)$$

where n is the iteration number, and i, j enumerate the nodes along the x and y -axes, respectively.

Due to symmetry of the problem, half of the domain in Figure 1 has been solved. The boundary conditions are:

$$\tilde{\eta}|_{\tilde{x}, \tilde{y} \in \text{anode edge}} = \tilde{\eta}_0, \quad \tilde{\eta}(\tilde{X}, \tilde{y}) = 0, \quad \frac{\partial \tilde{\eta}}{\partial \tilde{y}} \Big|_{\tilde{y}=0} = \frac{\partial \tilde{\eta}}{\partial \tilde{y}} \Big|_{\tilde{y}=\tilde{Y}} = 0 \quad (5)$$

Here, \tilde{X}, \tilde{Y} represent the size of the computational domain in the Debye length (DL) units. The first condition in Eq. (5) fixes overpotential at the anode edge, the second one prescribes zero $\tilde{\eta}$ far from the anode, and the last two conditions mean zero y -component of proton current along the symmetry line $\tilde{y} = 0$ and along the top side of the computational domain. In PEM fuel cells, the deviation of $\tilde{\eta}$ from $\tilde{\eta}_0$ at the anode edge is small and here, we neglect it [3]. Zero overpotential at $\tilde{x} = \tilde{X}$ is an approximate condition, which is satisfied if \tilde{X} is sufficiently large (see below).

4 Results and Discussion

The anode shape is described by parabola

$$\tilde{x} = \alpha (\tilde{y}_{base}^2 - \tilde{y}^2) \quad (6)$$

where α is the tip curvature parameter, and \tilde{y}_{base} is the half-length of parabola baseline along the y -axis. The curvature of parabola is $k = 2\alpha$; two variants corresponding to $\alpha = 1$ and $\alpha = 100$ have been calculated. The parameter \tilde{y}_{base} has been chosen to provide in both variants the same tip prominence of 4 DL (Figure 2).

Qualitatively, in both panels of Figure 2, the overpotential around the tip decays with the distance much faster, than close to the linear section of the anode edge. However, the characteristic length of $\tilde{\eta}$ decay around the tip is nearly the same on the top and bottom panels. Figure 3 shows the axial shapes $\tilde{\eta}(\tilde{x}, 0)$ for the anode curvatures of 2 ($\alpha = 1$) and 200 ($\alpha = 100$). As can be seen, near the sharp tip with $\alpha = 100$, $\tilde{\eta}$ decays with \tilde{x} faster, than near the tip with $\alpha = 1$; however, the difference between the two curves is rather marginal. Analytical solution for the radial shape of overpotential near the circular anode shows that the characteristic length of $\tilde{\eta}$ decay depends on the anode radius logarithmically. Numerical solutions for the parabolic tip in Figure 2 exhibit similar trend.

Most important, however, is that the shapes near the anode tip are much steeper, than the Gouy–Chapman shape of overpotential near the straight anode edge (Figure 2). To provide a good accuracy of measurements, the reference electrode (RE) should be located at the point, where $\tilde{\eta}(\tilde{x}, 0) \simeq 0$. As can be seen, this point is achieved at the distance of about 2 DL from

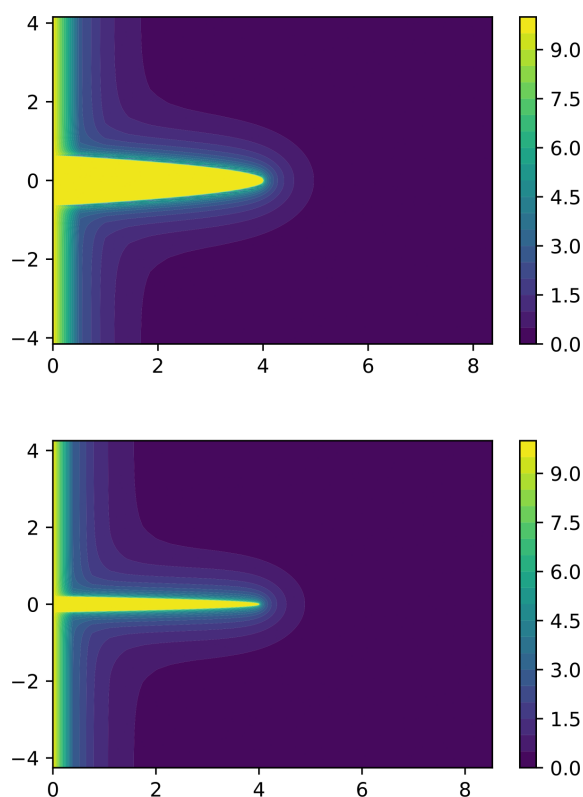


Fig. 2 Contour lines of the dimensionless ORR overpotential $\tilde{\eta}$ around the anode with the curvature 2 (top panel) and 200 (bottom panel). In both the panels, the tip prominence is 4 Debye length (DL) units and the scales are given in the DL units. The ORR overpotential in the working domain $\tilde{\eta}_0$ is 10, which corresponds to the dimension $\eta_0 \cong 300$ mV.

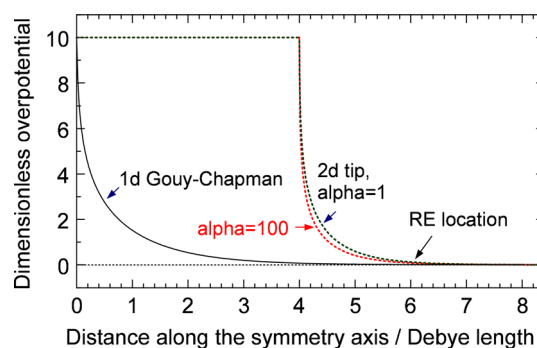


Fig. 3 Dotted lines – the shapes of the ORR overpotential along the symmetry axis \tilde{x} of the problem. The anode tip is located at $\tilde{x} = 4$. Blue curve corresponds to the anode curvature parameter $\alpha = 1$, red curve is for $\alpha = 100$. For comparison, the one-dimensional shape of Gouy–Chapman potential at the planar anode edge located at $\tilde{x} = 0$ is shown. The rightmost arrow indicates possible location of the reference electrode at the distance $\cong 2$ DL from the anode tip. Note that at the planar anode edge, the reference electrode should be positioned at the twice larger distance of $\cong 4$ DL (see the 1d Gouy–Chapman curve).

the tip, while in the case of a straight anode edge, a comparably small value of $\tilde{\eta}$ is reached at the twice larger distance (4 DL, Figure 2).

In physical units, the Debye length of the problem is given by Eq. (3). With the typical data for PEM fuel cells ($b = 0.03$ V, $\sigma_m = 0.1$ S cm^{-1} , $l_t = 10^{-3}$ cm, $l_m = 2.5 \cdot 10^{-3}$ cm, $i_* = 10^{-3}$ A cm^{-2}), this length is about 2.7 cm. Thus, the RE can be located near the sharp anode tip at the distance of about 5.5 cm. This value is quite acceptable in automotive stacks with the typical cross section of 10×10 to 20×20 cm, taking into account that the system “anode tip + RE” can be designed, as shown in Figure 4.

The model assumes uniformity of the ORR overpotential η through the CCL depth. In case of severe proton or oxygen transport limitations in the CCL, this condition is not fulfilled and the x -shapes of η and Φ would be quite different from those obtained above. However, at a large distance

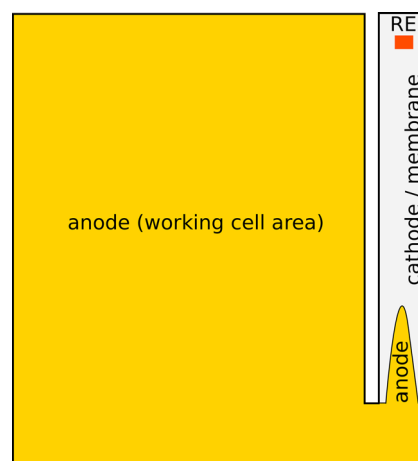


Fig. 4 A compact design of the reference electrode (RE) positioning at the anode tip, cf. Figure 1.

from the anode tip, η would still tend to zero and Φ would tend to some average ORR overpotential in the working cell area.

5 Conclusions

A 2D model for the distribution of the ORR overpotential η around the planar parabolic anode edge is solved numerically. The solution shows that η decays down to nearly zero at the distance on the order of two Debye length λ_D of the problem. At this point, the membrane potential reaches the value of ORR overpotential in the working cell area. Therefore, by placing the reference electrode at the distance of $2\lambda_D$ from the anode tip, it is possible to measure the working ORR overpotential in PEM fuel cell. With the typical PEM fuel cell parameters, this distance is about 5.5 cm. A possible reference electrode positioning in a large-scale cell is suggested.

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